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MODERN CHEMICAL PROCESSES

A Series of Articles Describing Chemical Manufacturing Plants

by the Editors of
Industrial and Engineering Chemistry
in conjunction with the technical staffs
of the cooperating organizations

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VOLUME IV

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FOREWORD

With this fourth volume of "Modern Chemical Processes," the editors of *Industrial and Engineering Chemistry* and the Reinhold Book Division feel that it is getting to be a habit. It is a good habit, judging from the demand for the volumes. Volumes I and II have been through a second printing, Volume III is expected to exhibit the same pattern. Volume IV brings up to 88 the number of detailed descriptions of operating plants in the chemical process industries.

In previous editions we have indicated in some detail the philosophy behind the Staff-Industry Collaborative Reports in *Industrial and Engineering Chemistry,* and the rigid requirements which are maintained. It is because of these high standards that Volume IV of "Modern Chemical Processes" contains a few less than a full two-year complement of these articles.

Staff-Industry Collaborative Reports continue to be one of I&EC's most widely and regularly read features. The companies who participate invariably are more than satisfied with the final form in which these reports appear. Some of them are repeaters several times over—we have no policy which precludes publication in collaboration with authors from the same company more than once, providing the story can be based on a different plant, a different process, or a new approach, either in techniques or equipment, to an old process.

We wish to thank again the many collaborating authors and company officials who have made this series and this and preceding volumes of "Modern Chemical Processes" possible, and our own regional editorial staff who have done the major job of writing.

WALTER J. MURPHY
Editorial Director

Washington, D. C.
March 1, 1956

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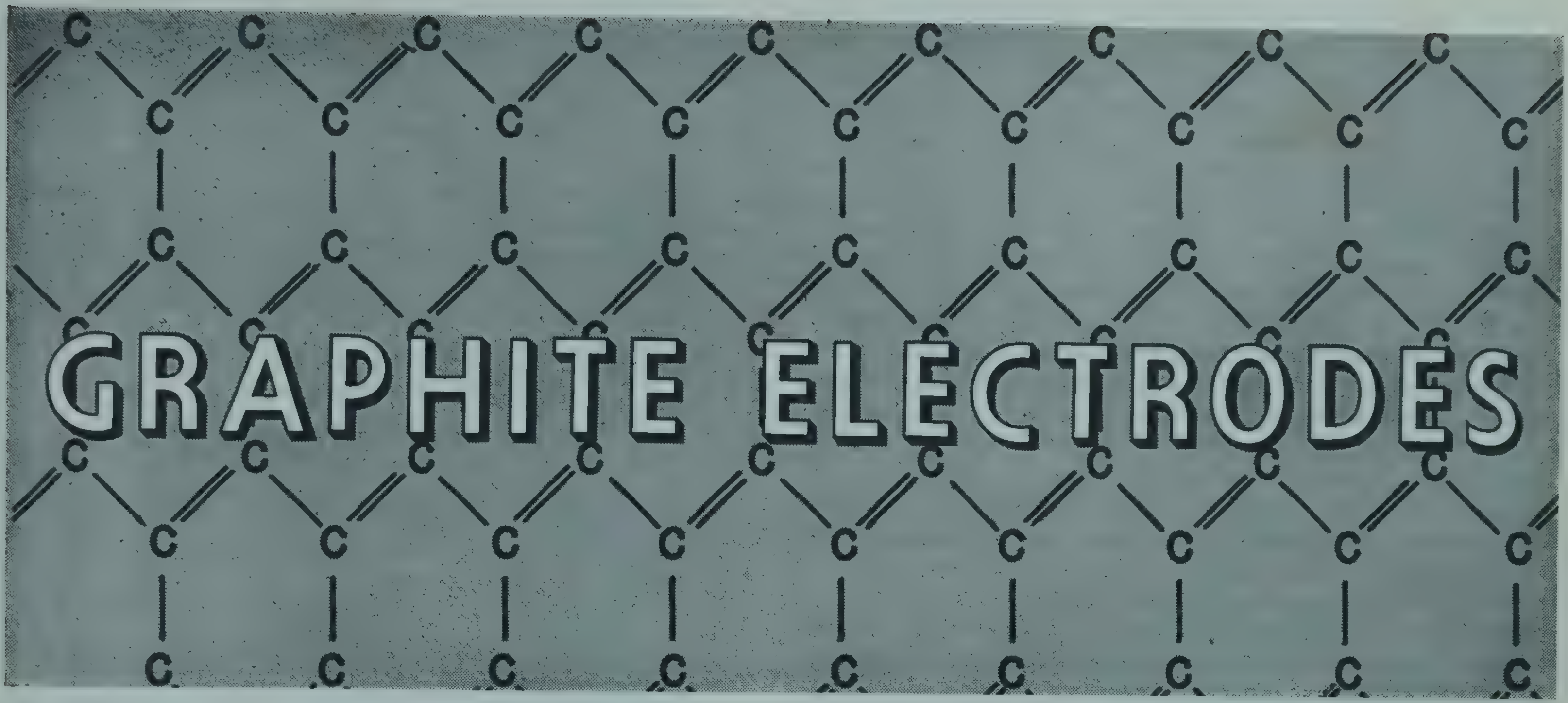
GRAPHITE ELECTRODES



RODNEY N. HADER
Associate Editor
In collaboration with

B. W. GAMSON
Great Lakes Carbon Corp., Morton Grove, Ill.

BRUCE L. BAILEY
Electrode Division, Great Lakes Carbon Corp., Niagara Falls, N. Y.

THE production of "synthetic" graphite by the electric furnace method is among the oldest of the chemical process industries in this country, having been founded just shortly before the turn of the century. And while it is not a match in age for the manufacture of sulfuric acid (perhaps our oldest commercial chemical endeavor and long considered an accurate barometer of over-all business activity), this industry—and especially that segment devoted to the production of graphite electrodes—has become so infused in chemical and metallurgical process industries that one familiar with electrode markets can use them like sulfuric acid sales, to gage general industrial activity.

Synthetic graphite's conductivity, combined with excellent refractoriness and resistance to thermal shock, makes it an electrode material without peer. The continued expansion of electric furnace operations and the trend toward larger furnaces and higher inputs of power have led to the production of the large high quality electrodes in use today. Graphite lends itself similarly to use as a material for the construction of crucibles and as a permanent mold material in the casting of metals. Virtually inactive chemically, it finds excellent application as an anode material in the electrolytic production of chlorine, sodium, caustic soda, and chlorates, as well as in the manufacture of piping and structural members for heat exchangers, reaction towers, and acid absorbers.

Graphite and amorphous carbon shapes, because of the methods that must be used in their manufacture, average 20 to 30% porosity. In applications where this porosity is undesirable, special treatments can be employed to render the materials impervious to gases or liquids. Porosity is not normally a disadvantage in metallurgical applications, since most liquid metals do not wet graphite at temperatures ordinarily encountered.

Graphite occurs in nature in fair abundance. Deposits are known all over the world, and the natural product has been used for ages in various applications. However, the natural product is usually quite impure, and beneficiation often makes it expensive. In addition, the strength of bodies formed from natural graphite is often rather poor. When the electric power industry was in its infancy, the need for formed pieces of graphite not readily prepared from the natural product soon appeared, with the result that experimental work aimed at graphite synthesis was begun. The experimentation was definitely successful, leading to the development of a synthetic material containing small crystals in a random arrangement that provides strength in all directions.

In 50 Years, Electric Furnace Capacities Have Increased from 1 to 150 Tons per Batch

Increasing industrialization, with its attendant requirements for handling more corrosive materials at higher temperatures and pressures, led to the need for structural materials other than carbon steel. The metallurgical processes for producing the alloys that were developed required close control, best accomplished by the use of the electric furnace. Early furnaces produced about 1 ton per batch and used electrodes, perhaps 4 inches in diameter, with a current-carrying capacity of about 1000 amperes. Today the largest furnaces hold 150 tons or more of alloy per batch, producing this amount in as little as 4 hours. Power inputs have been increased to the vicinity of 35,000 kva. through the use of synthetic graphite electrodes 20 to 24 inches in diameter, up to 96 inches long, and weighing over a ton each. The current-carrying capacities of some of these electrodes range from 35,000 to 45,000 amperes.

Production of new structural materials such as magnesium and titanium is heavily dependent on high quality synthetic graphite electrodes. Amorphous carbon electrodes offer similar advantages in the electric furnace methods used to produce calcium carbide, elemental phosphorus, and ferroalloys. For these applications, electrodes up to 48 inches in diameter and weighing as much as 4 tons each are available. The curve in Figure 1, in which estimated values of annual synthetic graphite production are plotted for the past half century, indicates the rapid rate of growth the industry has experienced in recent years. Similar growth has occurred in other industrial nations (*7*).

The history of commercial production of synthetic graphite electrodes dates from June 1897, when the first furnace load, consisting of 2905 small electrodes ($^{7}/_{8} \times 1^{1}/_{4} \times 15$ inches) totaling 2300 pounds in weight, was graphitized in a Carborundum Co. furnace under the supervision of E. G. Acheson, to whom a patent had been issued in 1896 (*1*). That first commercial operation was sufficiently successful that during the remainder of 1897 a total of 142,000 pounds of electrodes was graphitized (*6*).

The discovery that graphite can be produced in an electric furnace resulted from an earlier discovery of a method for manufacturing silicon carbide. In studying the effects of high temperatures on this compound, it had been observed that at high temperatures it was decomposed; silicon was vaporized, and the carbon remained behind not in an amorphous but in a graphitic form. Acheson pursued this lead to develop a commercial process for graphite production based upon anthracite coal.

The graphitizing process itself has not been changed in essence since it was first discovered; rather, improved techniques in various manufacturing steps have permitted the production of superior products in ever-increasing size and variety. From a very limited market for a few products such as small electrodes, crucibles, arc rod carbons, and specialty items, the industry has branched out to produce a range of useful materials that have actually led in some cases to the founding of new key industries. An example is the electric furnace steel industry, already responsible for the major portion of high alloy steel production, and now promising keen competition for the open hearth process in the large scale manufacture of ordinary steel (*2*).

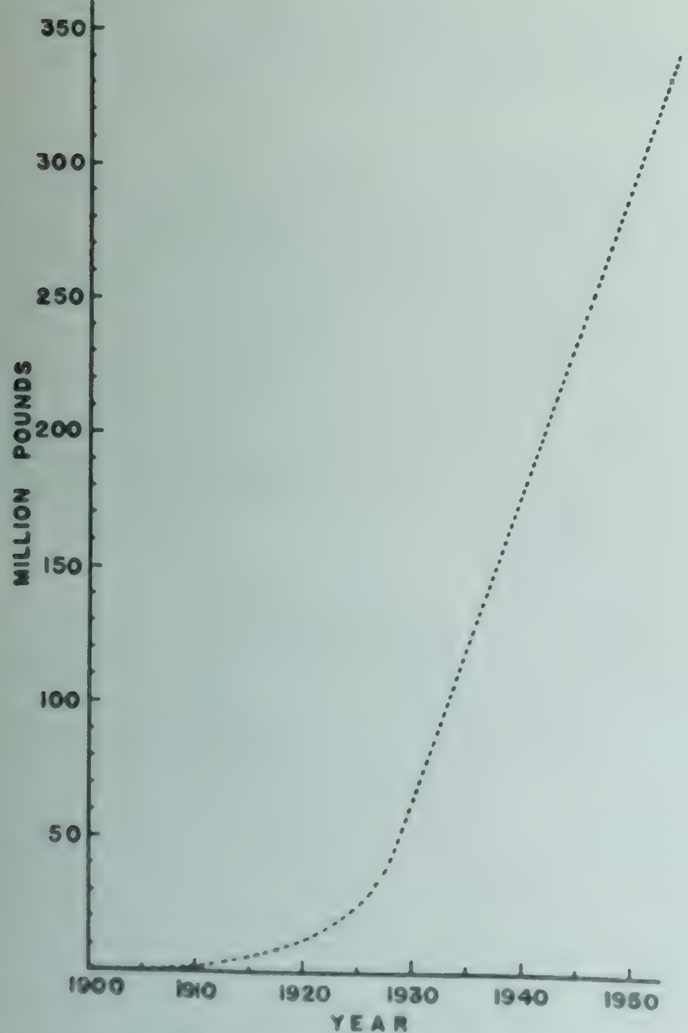


Figure 1. Estimated Production of Synthetic Graphite in the United States—1900 to date

Table I. Properties of Typical Raw Materials for Graphite Electrode Manufacture

	Calcined Petroleum Coke	Coal Tar Pitch	Impregnating Pitch	Extrusion Lubricant
Real density, grams/cc.	2.00–2.10	..	..	..
Sulfur, %	0.5–4.0	0.2–0.5	0.2–0.5	..
Ash, %	0.3–1.5	0.2–0.5	0.2–0.5	..
Softening point, ° C.	..	99–101	90–95	..
Benzene insolubles, %	..	29–32	12–15	..
Specific gravity, 60° F./60° F.	..	1.29–1.32	1.25–1.29	0.85–0.95
Viscosity, cp.				
At 160° C.	..	450	150	..
At 100° C.	..	..	..	9–37
Coking value[a], %	..	60	40	..

[a] In electrode manufacture.

While basic processes have not changed radically over the years, there has been a major evolution in raw materials sources and production technology. The industry in its early days operated with anthracite coal, wood charcoal, or coal beneficiated to lower its ash content; little attention was given to the uniformity of the carbon used or the pitch employed as binder. With the development of applications technology, however, sources of carbon of controlled purity became increasingly important, until finally the industry standardized on petroleum coke—the purest form of industrial carbon available in large quantities. Petroleum coke has been the chief source of electrode carbon since about 1918, and both coke and binder pitch are now required to meet rigid specifications in chemical and physical properties. Typical properties of raw materials currently in use are given in Table I.

The growth of the electrode industry, especially in the size of products made, has necessitated a continuous development of its manufacturing techniques. Major improvements have been made in extrusion press design, baking furnaces, and graphitizing units. The successful operation of large graphitizers has occurred with the cooperation of the electrical equipment producers since new designs in transformer size and bus-bar systems were required. These equipment developments have also extended to machining operations.

Chemically, Electrodes Are Essentially Pure Carbon

The conversion of amorphous carbon to graphite was first believed to involve the formation of intermediate carbides, generated through the reaction of the carbon with minerals and metallic oxides present as impurities. The graphite crystallites were believed to be formed through decomposition of the carbides at high temperatures.

While it is recognized that graphite can be formed by the thermal decomposition of carbides, current theories regarding the conversion of amorphous carbons to graphite do not acknowledge intermediate carbide formation as an essential element in the mechanism (*3*). Such carbonaceous materials as calcined petroleum coke are believed to contain groups of small, graphitelike crystallites with a proportion of unorganized carbon, presumably attached to the edge atoms of the graphitelike layers and linking the crystallites one to another. On further heating, thermal recrystallization causes the graphitelike crystallites to grow at the

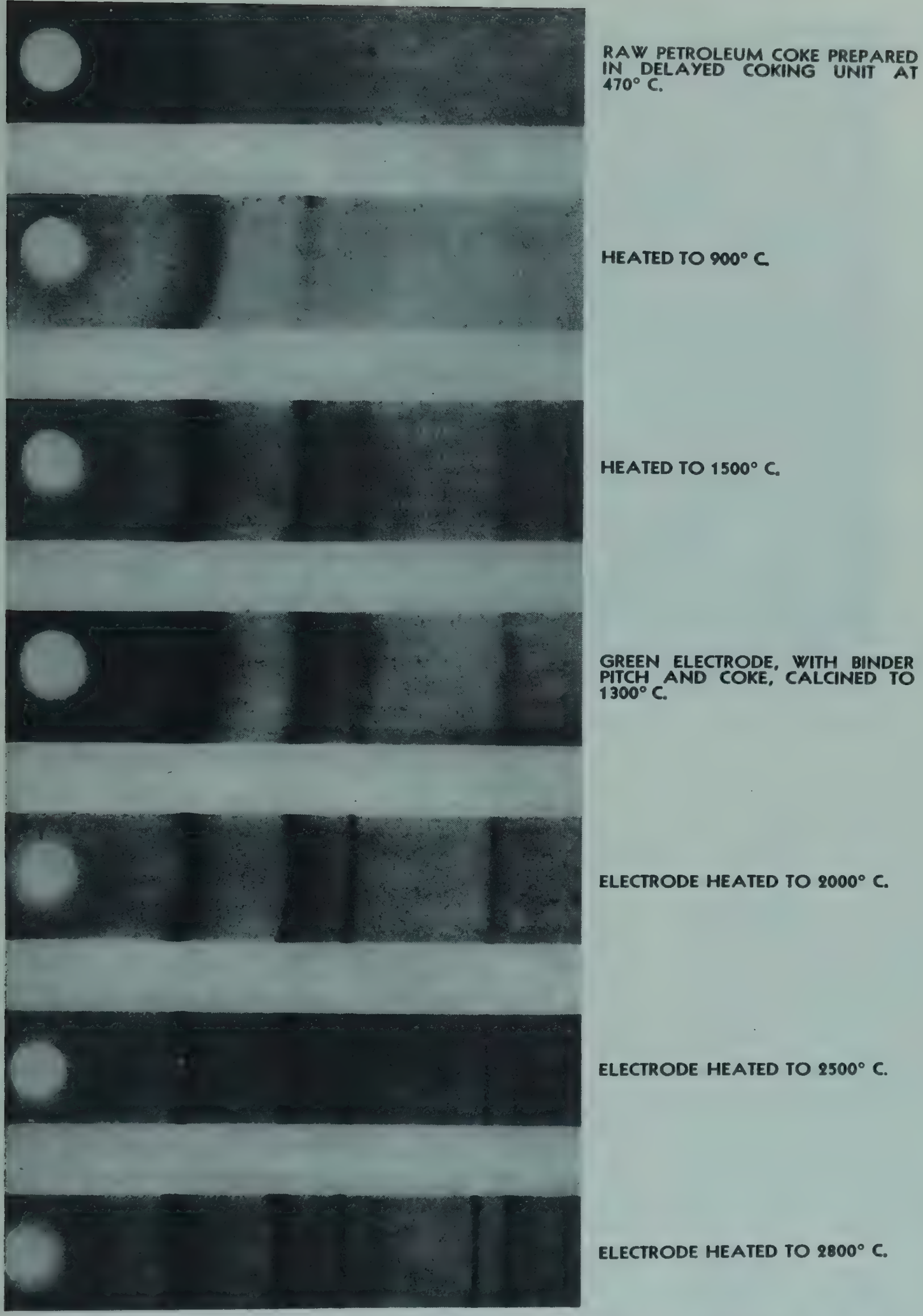


Figure 2. Growth of Crystallites in Graphite Synthesis as Indicated by X-Ray Diffraction Patterns

expense of the unorganized carbon. Once the unorganized carbon has been consumed, further growth occurs by gradual movement of whole layers or even groups of layers, and not by addition of isolated atoms or small groups of atoms. This progression in the growth of graphitelike crystallites is vividly demonstrated by the series of x-ray diffraction patterns shown in Figure 2.

The top pattern of "raw coke" contains only two visible reflections—both are diffuse, and one is very weak. The small angle scattering around the central spot is pronounced. With increasing temperature of heat treatment the appearance of higher order reflections with a progressive sharpening of the lines is observed. The pattern for the green electrode resembles that of the petroleum coke from which it was prepared, except that the presence of the binder has given rise to a greater amount of small angle scattering. As the temperature of the heat treatment increases within the graphitizing range (beginning at about 1600° C.) a further sharpening of previously visible reflections as well as the appearance of additional higher order reflections is observed. These transformations in the x-ray patterns attend the growth and mutual orientation of the graphite crystallites.

The impurities that occur in the raw materials for synthetic graphite production are eventually almost entirely removed by distillation. For the most part these impurities, present in the form of minerals and metallic oxides, are converted to carbides and subsequently decomposed as furnace temperatures reach high enough levels to distill the elements from the system. Tables II and III show thermodynamic relationships for typical impurities found in the raw materials for electrode manufacture, or formed during the baking or graphitizing cycles. Since virtually all such impurities are vaporized during processing, it might appear that the presence of relatively large amounts of impurities is unobjectionable; however, the amount of ash in a given coke may strongly influence the physical properties of the finished graphite made from it. Table IV presents typical physical properties for a graphite mold stock, 20-inch diameter electrode, graphite electrolytic anode, porous carbon, and porous graphite, all based on petroleum coke. Chemically, all are essentially pure carbon, analyzing 99 to 100% carbon.

Virtually all synthetic graphite production in this country is at present divided among three major producers, Great Lakes Carbon Corp., International Graphite & Electrode Corp., and National Carbon Co., Inc. Of these, Great Lakes is the the most recent entry into the field.

Prior to 1940, the principal business of Great Lakes Carbon Corp. (then known as Great Lakes Coal and Coke) was calcining refinery coke. As a natural step toward integration, Great Lakes entered the electrode field, establishing its electrode division to handle production and sales of graphite and amorphous carbon electrodes and related carbon products.

The division's first plant, established at Niagara Falls, N. Y., is still in operation both as a producing unit and as a center for technical development and service activities. Specialized products such as amorphous carbon cement for use as cathodic lining in aluminum pots are also produced at Niagara Falls. Most basic research for the division is conducted at the company's laboratories at Morton Grove, Ill., where research for all Great Lakes divisions is centered.

Morganton, N. C., Plant of Great Lakes Carbon Co. Produces Electrodes from Petroleum Coke and Coal Tar Pitch Binder

Operator Samples Air-Cooled Mixture as It Pours from Cooler to Extrusion Press

The Morganton, N. C., plant of Great Lakes electrode division is one of the most modern integrated electrode plants in the world; it produces a complete line of synthetic graphite products. When current expansions are completed, this plant will turn out over 60,000,000 pounds of synthetic graphite products per year. Built for the Federal Government in 1943 as a war plant, the installation was purchased in 1947 by Great Lakes, and reactivated in the first quarter of 1949.

As shown in Figure 3, the principal steps in the manufacture of graphite electrodes are the preparation, weighing, and mixing of raw materials, extrusion of the heated mixture in desired shapes and cross sections, baking in gas-fired furnaces, and graphitizing in electric furnaces. The final product is a high purity, electrically conductive material, relatively soft and readily machined. Most graphite electrodes are produced as round cylinders, bored and threaded at each end to permit the successive addition of new lengths, forming essentially continuous electrodes.

Principal raw materials are a high purity carbon, primarily petroleum coke, and a highly aromatic binder, usually coal tar pitch. A typical mixture consists of about 40 parts of one or more sizes of screened petroleum coke particles, about 60 parts of fine petroleum coke flour, and about 30 parts of coal tar pitch as binder. The larger electrodes contain coke particle fractions as large as one half inch on three mesh, while the smaller electrodes may contain particles as small as through 20 on 35 mesh. Table V shows the relative proportions of various sizes of coke particle fractions and pitch binder content for typical formulations of mold stocks, anodes, and electrodes in various sizes.

Calcined petroleum coke from any of several silos, each of 450 tons capacity, is passed through a hammer mill (*1E*), and the particles are sized by means of vibrating screens (*4E*). Each size is discharged to an individual bin above the weighing floor, permitting gravity flow into weighing hoppers. Fines produced in the crushing and screening operation are passed through a ring-roller suction mill (*5E*) which further comminutes the particles until 52 to 55% will pass through a 200-mesh screen. Since the fines fraction is generally too small to provide enough flour, some crushed coke is added to provide the desired proportion of flour. The mill's built-in air classifiers automatically return oversized particles for further grinding. Material of suitable size is collected in the unit's bag filters and transferred to flour bins above the weighing floor.

The coal tar pitch used as binder is received in solid form and is crushed (*6E*) to a particle size of 1/4 inch or smaller. Graphite electrodes and amorphous carbon electrodes are made with the same kind of pitch. The crushed material is stored in bins above the weighing floor; only small quantities are crushed and

Table II. Thermodynamic Properties of Impurities in Synthetic Graphite Manufacture

Element or Compound	Melting Point, ° C.	Boiling Point, ° C.	Heat of Vaporization, Kcal./Mole	Heat of Formation (ΔH_{298}), Kcal./Mole	Free Energy of Formation (ΔF_{298})[a], Kcal./Mole
Fe	1539	2750[b]	84.2[b]	[c]	[d]
Ca	850	1690	38.6	[c]	[d]
Ti	1725	> 3000	..	[c]	[d]
Al	660	2500	69.6	[c]	[d]
V	1750[b]	3000[b]	..	[c]	[d]
Si	1440	2630	72.6[b]	[c]	[d]
FeO	1371	..	..	−64.5	−59
CaO	2500[b]	3400[b]	..	−151.9	−144.4
TiO_2	1850	3000[b]	..	−219	−206
Al_2O_3	2020	3250	..	−400	−378
V_2O_5	..	..	..	−382	−350
SiO_2 (tridymite)	1713	3500[b]	..	−206.5	−193.6
Fe_3C	1840	..	..	+5.8	+4.8
CaC_2	2300	..	..	−14.1	−16.7
TiC	3250	4300[b]	..	−57	−56
Al_4C_3	> 2800	..	..	−44	−44
VC	2830	3900[b]	..	−28	−27
SiC	> 2700	..	..	−28	−27
FeS	1190	..	..	−22.9	−23.5
CaS	..	..	..	−114	−113

[a] ΔF_{298} is calculated from the expression $\Delta F = \Delta H - T\Delta S$, where $T = 298$; values of ΔH and ΔS from Kubaschewski and Evans (*5*).

[b] Estimated

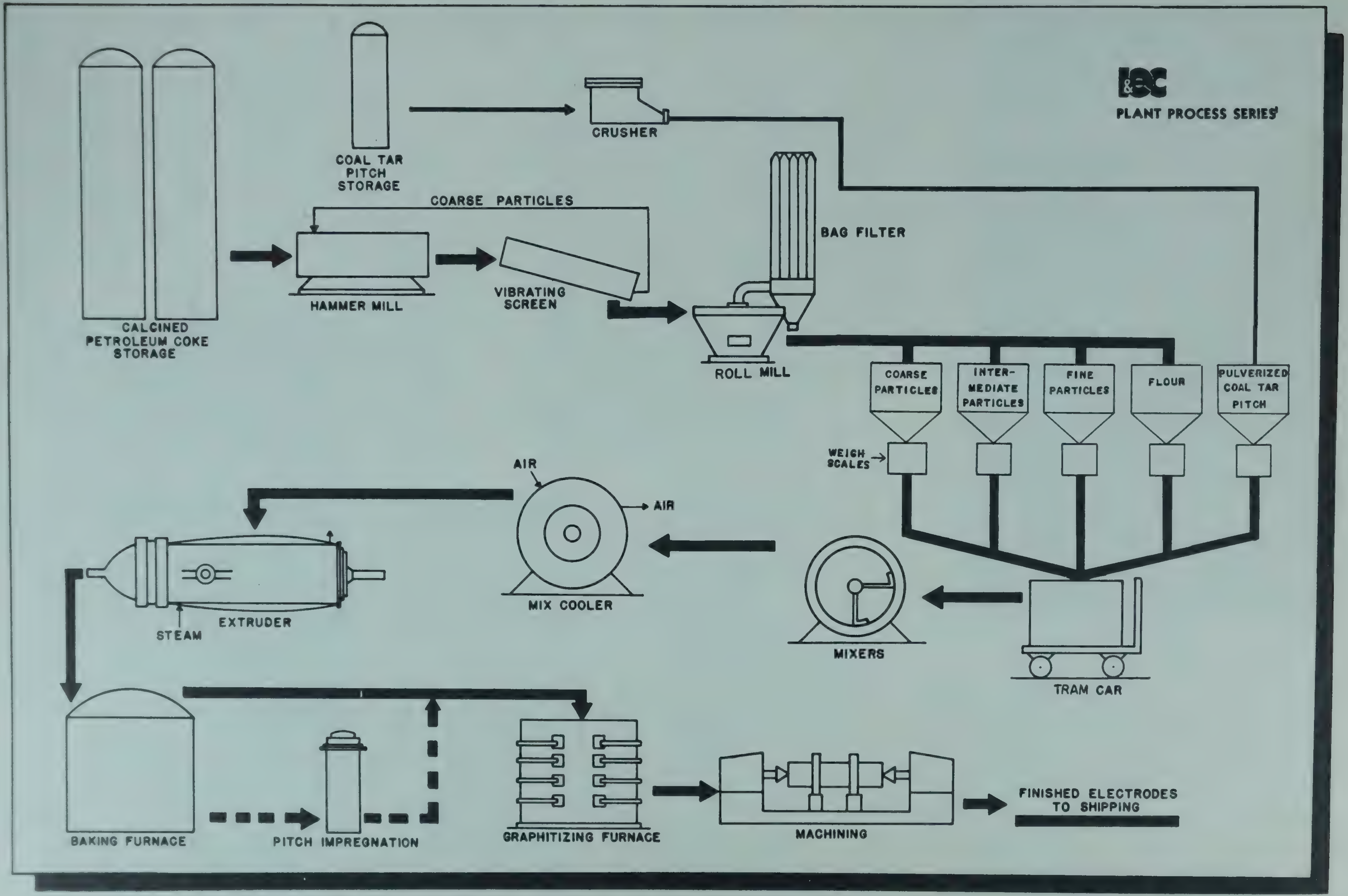
[c] Heat of formation of the elements is zero

[d] Free energy of formation of the elements is zero

Table III. Free Energy Changes for Reactions of Impurities in Synthetic Graphite Manufacture

Reaction	ΔF, Free Energy of Reaction, Kcal./Mole	Temp Range, ° K
$3FeO + 4C = Fe_3C + 3CO$	$110{,}300 - 14.95\,T\log T - 69.9\,T$	300-1640
$Fe_3C(\alpha) = 3Fe(\alpha) + C$	$-4{,}255 + 14.95\,T\log T - 37.8\,T - 3.35 \times 10^{-3}\,T^2$	300-1640
$2Al_2O_3 + 9C = Al_4C_3 + 6CO$	$566{,}300 - 257\,T$	300–2300
$Al_4C_3 = 4Al(s) + 3C$	$43{,}300 + 1.8\,T$	300–930
$TiO_2 + 3C = TiC + 2CO$	$109{,}000 + 3.46\,T\log T - 93.3\,T$	300–2000
$TiC = Ti + C$	$57{,}000 - 2.75\,T$	300–2000
$CaO + 3C = CaC_2(\beta) + CO$	$112{,}000 - 53\,T$	300–2500
$CaC_2(\beta) = Ca(l) + 2C$	$14{,}600 + 5.88\,T$	1123-1963
$SiO_2 + 3C = SiC + 3CO$	$126{,}900 - 83.8\,T$	300–1700
$SiC = Si(s) + C$	$28{,}000 - 1.9\,T$	300–1700

Sources: Kelley (*4*) and Kubaschewski and Evans (*5*)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AIR
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STEAM
MIXERS
TRAM CAR
BAKING FURNACE
PITCH IMPREGNATION
GRAPHITIZING FURNACE
MACHINING
FINISHED ELECTRODES TO SHIPPING

Figure 3. Flow Sheet for Production of Synthetic Graphite Electrodes at Morganton, N. C., Plant of Great Lakes Carbon Corp.

Table IV. Physical Properties of Typical Synthetic Graphite Products from Petroleum Coke

	Mold Stock			20-Inch Diameter Electrode			Graphite Electrolytic Anode (Up to 2 × 9 Inch Cross Section)	Porous Carbon	Porous Graphite
	Green	Baked	Graphite	Green	Baked	Graphite			
Apparent density, g./cc.	1.70	1.60	1.70	1.65	1.57	1.54	1.56 – 1.66	1.05	1.05
Real density, g./cc.		2.09	2.24	..	2.09	2.24	2.24	2.09	2.24
Resistivity, ohm-inch									
Longitudinal	..	0.0020	0.00038	..	0.0023	0.00035	0.00035	0.006	0.001
Transverse	..	0.0030	0.00045	..	..	..	..	..	.
Modulus of rupture, lb./sq. inch									
Longitudinal	..	2600 (approx.)	2600	..	1100 (approx.)	1100		..	..
Transverse	.	2200 (approx.)	2200	..	900 (approx.)	900	..	..	..
Tensile strength, lb./sq. inch									
Longitudinal	..	1500 (approx.)	1500	..	575 (approx.)	575	700 – 1000	180	110
Transverse	..	1300 (approx.)	1300	..	..	..	..	..	..
Compressive strength, lb./sq. inch	..	8000 (approx.)	6000 (approx.)	..	4000	3000	4000	830	500
Porosity, %	..	22	24	..	24.5	31.2	30	50	53
Maximum particle size, inch	0.03 (–20 mesh)	0.03 (–20 mesh)	0.03 (–20 mesh)	..	..	..	100% Flour	..	..
Permeability to air, ml./cm./g./min.	..	..	..	..	..	..	..	5–500	5–500
Coefficient of thermal expansion, 10^{-7} inch/inch/° F.									
Longitudinal	..	21	14	..	15	10	11	27	21
Transverse	..	27	18	..	20	15	16	..	..
Modulus of elasticity (longitudinal), lb./sq. inch	..	..	1.2×10^6	..	1.5×10^6	700,000	$1.1 - 1.3 \times 10^6$	400,000 (approx.)	300, 000 (approx.)
Thermal conductivity, B.t.u./sq. ft./ft./hr./° F.	..	5	85	..	9	65	75 – 85	1.4	45

stored in warm weather, since the pitch tends to resolidify at elevated temperatures.

To facilitate extrusion, small quantities of a petroleum-base oil are added to the raw mixture for both graphite and amorphous electrodes. A primary requirement for the oil is that it have a low miscibility with pitch, in order that it may remain on particle surfaces where lubrication is most important.

"Green" Electrodes Are Extruded in Numerous Sizes and Cross Sections

Electrode production is essentially a batch process, although some steps are handled on an essentially continuous basis. Each batch of coke-pitch-oil mixture is weighed separately into a monorail car that holds about 600 pounds. The properly proportioned batch is dumped through a hole in the floor into a horizontal steam-jacketed mixer (*3E*) on the floor below. Paddle-type agitators keep the batch thoroughly mixed during a 20-minute heating cycle. At the end of the cycle the batch temperature is about 150° C. Fifteen horizontal mixers in parallel are required to maintain an adequate rate of feed to the plant's single extrusion press.

At the end of the mixing and heating cycle, the mixer door is opened, permitting the mix to be discharged onto a conveyor belt that leads to a cooler. Normally about four mixers are discharged simultaneously to provide a full charge for one of the coolers. Two coolers are used in parallel. The cooler (*2E*) is a rotating tumbler, somewhat similar to a concrete mixer in design. As the cooler rotates, air is drawn through it by a suction fan; the mix is tumbled in the cooler until its temperature is lowered to about 100° C. When the proper temperature is reached, the cooler batch is discharged into a chute that leads to the extrusion press.

The press (*7E*), with interchangeable dies for the production of electrodes in all sizes and cross sections, contains an extrusion cylinder or "mud chamber" about 3 feet in diameter. Mounted on heavy trunions, the cylinder can be rotated through an angle of 90°. It is turned to the vertical position to receive the cooled mix from the cooler's chute. A vertical tamping ram compacts the mix in the cylinder, after which the tamp is withdrawn and the cylinder is rotated to the horizontal position for operation. A hydraulic ram then enters the cylinder forcing the mixture under a pressure of 500 to 2500 pounds per square inch (depending upon die size) through the extrusion die. The entire press, including the die, is steam-jacketed. The extruded stock, still at approximately 100° C., is cut to length by means of a knife or taut wire, and discharged on a flat table.

Small electrodes are set aside at this point for air cooling, while larger sizes are rolled down a slight incline into a water bath. After an hour or more in the bath, with water at 25° C., the electrodes are removed for inspection of quality.

After inspection, the satisfactory pieces, now known as "green" electrodes, are either stored or sent immediately to the baking furnace. Care is exercised to prevent exposure of the stored

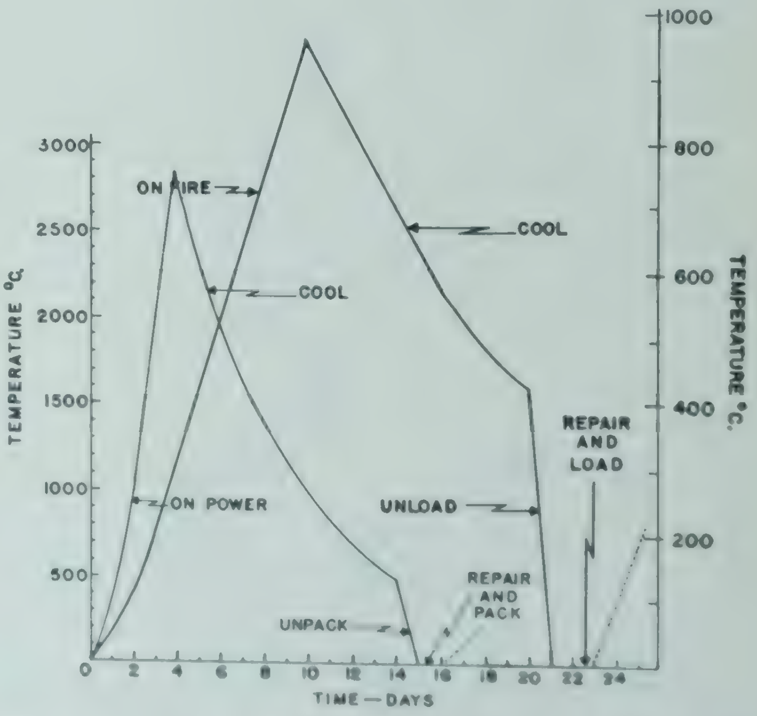


Figure 4. Typical Temperature Cycles for Baking and Graphitizing Furnaces

Giant Electrode Rolls into Cooling Trough as Another Issues from Extrusion Press

Table V. Proportions of Dry Ingredients for Preparation of Typical Graphite Products

	Parts Screened Petroleum Coke Particles			Parts Petroleum Coke Flour, 55% through 200 Mesh	Parts Coal Tar Pitch
	Through ½ inch on 3 mesh	Through 10 on 20	Through 20 on 35		
Graphite mold stock	..	..	50	50	34
Intermediate electrode, 10–20 inches diameter	..	25	15	60	32
Large electrode, 20–24 inches diameter	20	10	10	60	30
Anode or small electrode	..	..	..	100	36

electrodes to high temperatures, since the pitch binder tends to soften at elevated temperatures, causing distortion and rejection by the inspection department.

They Are Baked at Internal Temperature of 950° C.

The gas-fired baking furnaces are brick-lined chambers 10 × 30 × 11½ feet deep. For the baking operation, large electrodes are stationed vertically in the furnace, and smaller ones are placed in horizontal layers. In the furnace, electrodes are separated from one another by a packing material which consists of a mixture of sized petroleum coke and river sand. The furnace is loaded to a depth of several inches with packing material, upon which the electrodes are carefully spaced. Depending on size, the electrodes are placed from ¼ inch to 2 inches apart, with additional packing material in the interstices; electrodes are stacked layer upon layer until the furnace is nearly filled. A fairly thick layer of packing material is placed over the top. Thermocouples are inserted at several critical spots between electrodes, and the furnace is ready for operation.

The furnaces are fired with producer gas, manufactured in an adjacent building on the plant site. After a maximum temperature of about 950° C. (within the electrodes) has been reached, firing is discontinued. When the furnace has cooled sufficiently, the top layer of packing is removed and the electrodes are pulled from the furnace for further cooling in air. Loose packing material is brushed from the electrodes, and each piece is visually inspected for cracks, chipping, severe bowing, or cross-sectional distortion.

After culling out defective pieces, normally amounting to 1 to 2%, samples are selected for measurement of diameter, length, weight, roundness, apparent density, and electrical resistivity. Acceptable baked electrodes are then either stored in piles or transferred directly to the graphitizing furnaces.

Electric Furnaces (at 2800° C.) Convert Coke into Graphite

In the graphitizing furnaces, electric current is used to heat the electrodes to a temperature of about 2800° C., a treatment that converts the relatively hard coke structure into soft, unctuous graphite. The electrodes themselves form the central part of the graphitizing furnace, with current flowing through as well as around them. The furnace loading is built up on a semipermanent brick bed 12 feet wide, 30 feet long, and 2 feet deep. A layer of fine carbon is spread over the bed as a base for the electrodes, which are then placed horizontally on the bed. The electrodes are separated by ¼ to 6 or 7 inches of "resistor" material. Spacing is adjusted according to the size of the electrodes under treatment.

The resistor material consists of a mixture of graphitized and ungraphitized coke particles. With the tiers of electrodes in place and surrounded by resistor material, concrete blocks are used to build up the outside walls of the furnace. These are placed about 2 feet away from the electrode ends, and the intervening space is filled with insulating material consisting essentially of sand and coke in the proportions required for the formation of silicon carbide. The insulation is recycled many times in the furnace, gradually building up a substantial silicon carbide content. The furnace loading step is completed by placing a layer of insulation about 2 feet thick over the electrode load.

Partially Dismantled Furnace Prior to Unloading Graphitized Electrodes

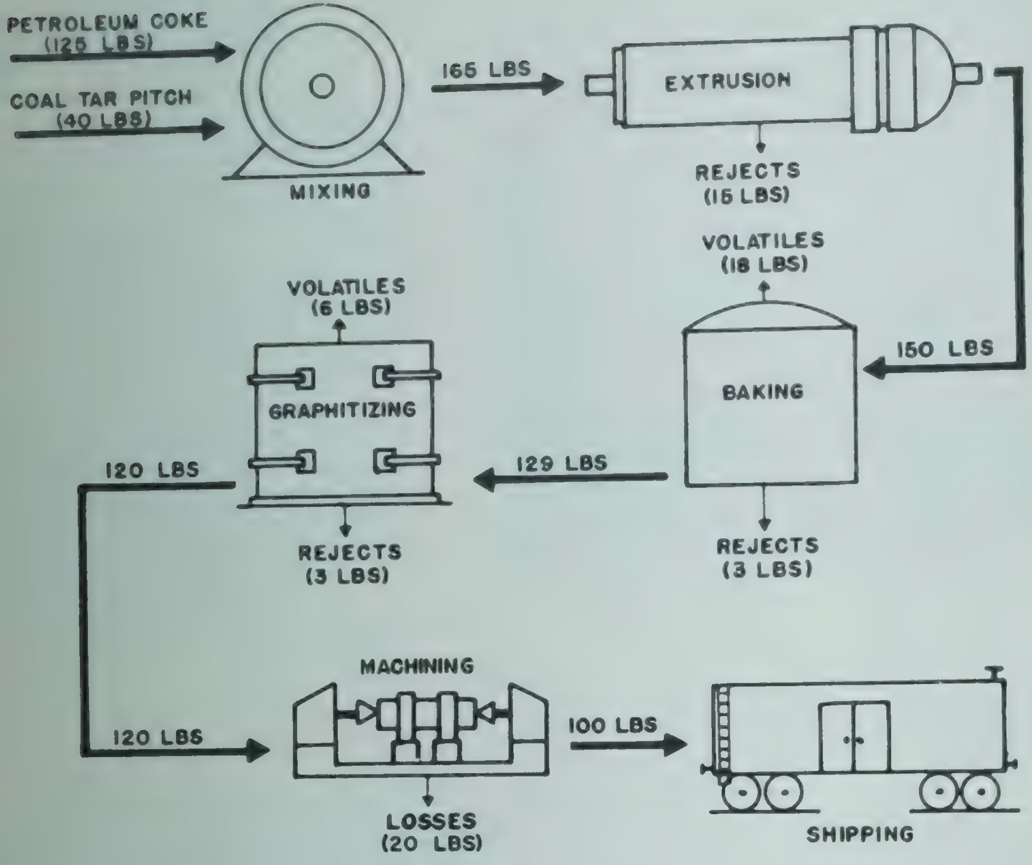
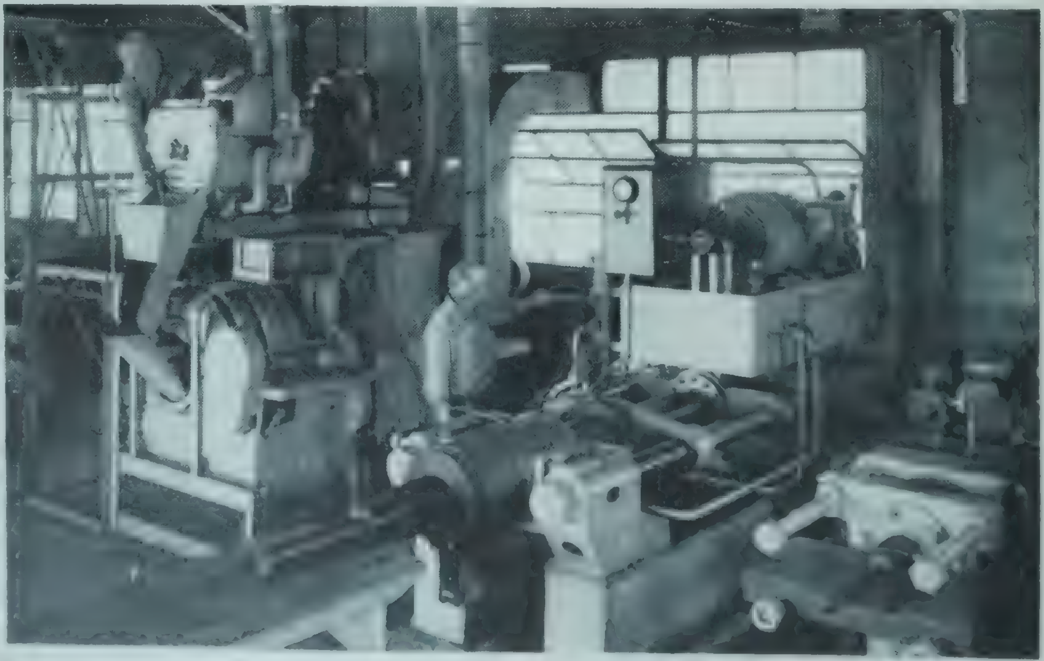


Figure 5. Simplified Flow Sheet Showing Materials Balance for Graphite Electrode Production

With the furnace thus ready for operation, electrical connections are made at the furnace ends, and the furnace heating cycle begins with the flow of electricity. The heating cycle lasts from 2 to 4 days; the end point is determined by the total energy consumption in kilowatt hours per pound of electrode. Again depending on electrode size, the total energy input ranges from 2.0 to 4.0 kw.-hr. per pound of baked electrode weight. Experience has shown that this amount of power will satisfactorily graphitize the electrode charge. Degree of graphitization is checked through measurement of resistivity and other properties of the graphitized electrodes on removal from the furnace.

At the end of the heating cycle, electrical contacts are removed, and the furnace charge is allowed to cool for about 10 days. During this period, insulation is gradually removed to accelerate cooling. When cool enough, electrodes are removed from the furnace by means of cable slings and are placed on steel rails for further cooling. Temperature cycles for typical runs in both baking and graphitizing furnaces are given graphically in Figure 4.

The cooled electrodes, cleaned by brushing or scraping, are inspected individually for defects such as cracks or distortions. Numerous samples are then measured for diameter, weight, roundness, length, bowing, electrical resistivity, and apparent density. In some cases, measurements of breaking strength, coefficient of thermal expansion, and Young's modulus are added. Electrodes that meet rigid quality specifications are stored for machining and shipment.



Experimental Extrusion Press at Great Lakes Carbon Corp., Niagara Falls, N. Y., Checks Flow Properties of Test Mixture

Almost All Graphite Electrodes Are Machined before Use

Machining of the electrodes includes facing the ends, boring and threading sockets for nipples, and carefully turning the curved surfaces. Semiautomatic lathes are used to achieve economical production rates for relatively large scale production volumes.

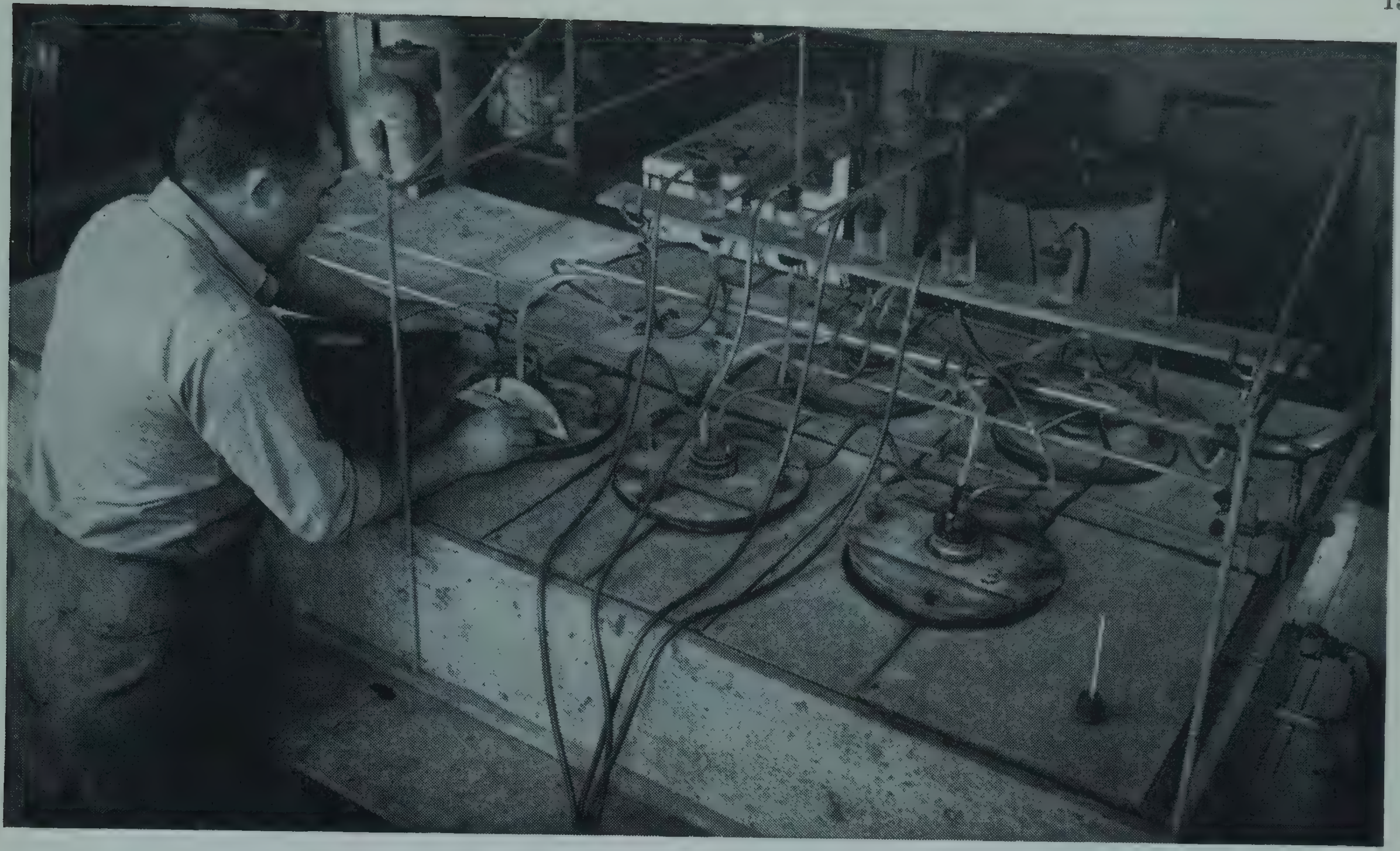
Tapered threads have largely superseded straight threads for electrodes and nipples, although the latter are still used to some extent. It is true that the tapered thread is more difficult to machine and requires closer tolerances, achieved only with more elaborate gaging equipment. When properly prepared, however, tapered threads give superior joints, and are much more easily assembled in the field.

Finished electrodes are normally shipped either in boxcars or in open gondolas. They may be braced by wood or band-strapped to prevent movement; recently there has been an increasing trend toward palletizing for shipment.

Since the electrodes are quite soft, special care must be taken to protect them against gouging and rubbing. Especially the ends, through which virtually all the current in an electrode flows, must be maintained smooth and clean, free from chips or contamination.

Process Requires 165 Pounds Raw Materials per 100 Pounds Finished Electrodes

The simplified flow diagram in Figure 5, showing a materials balance for electrode manufacture, indicates that the production



Miniature Chlorine Cell Tests Operating Characteristics of Experimental Graphite Anodes

of 100 pounds of finished electrodes, ready for shipping, requires 165 pounds of the principal direct raw materials. In addition, relatively large amounts of auxiliary materials must be handled during the manufacturing process. In the baking furnaces, for example, one pound of packing material is used for each pound of electrode in process. In the graphitizing furnace, about three times the weight of the electrode charge is added as insulation and resistor material, or about 2.6 pounds of insulation and 0.4 pound of resistor material per pound of electrodes. The total weight of the furnace load for a 50,000-pound charge of electrodes is thus approximately 200,000 pounds.

Electric power consumption for all processing needs varies from 2.5 kw.-hr. per pound of finished product for anodes and small electrodes to 3 kw.-hr. per pound for mold stock and intermediate (10- to 20-inch diameter) electrodes.

Consumption of coal for producer gas, used in the baking furnaces, varies from 0.3 to 1.0 pound per pound of finished electrode, depending upon whether the sensible heat in furnace flue gases is used for preheating other furnace charges. About 6 gallons of water is required for each pound of graphite. Of this amount, 45% is used in the graphitizing department, 30% in extrusion, 20% in baking, and 5% for miscellaneous plant uses. Water is used only once at the Morganton plant; there is no cooling pond.

The total number of hourly employees at the Morganton plant averages 350, including operating and control personnel. In addition, there are about 65 salaried employees at the plant.

Test Checks Control Size, Shape, Density, and Resistivity of Product

Great Lakes maintains an exhaustive system of inspection and testing checks, beginning with raw materials and extending even into the purchaser's plant. To make certain that flaws will be discovered at the earliest possible point in the sequence of production steps, every shipment of raw materials—coke, pitch, and oil—entering the Morganton plant is sampled and analyzed for conformance to specifications. At every stage thereafter in the manufacturing process, physical and chemical determinations are employed to eliminate faulty materials or specimens.

Through frequent sampling the coke milling machines are carefully controlled in order that the proper proportions of closely sized coke particles and flour fractions can be maintained. The particle size range of each coke fraction obtained from the screening operation is carefully checked by frequent sampling and screen analysis.

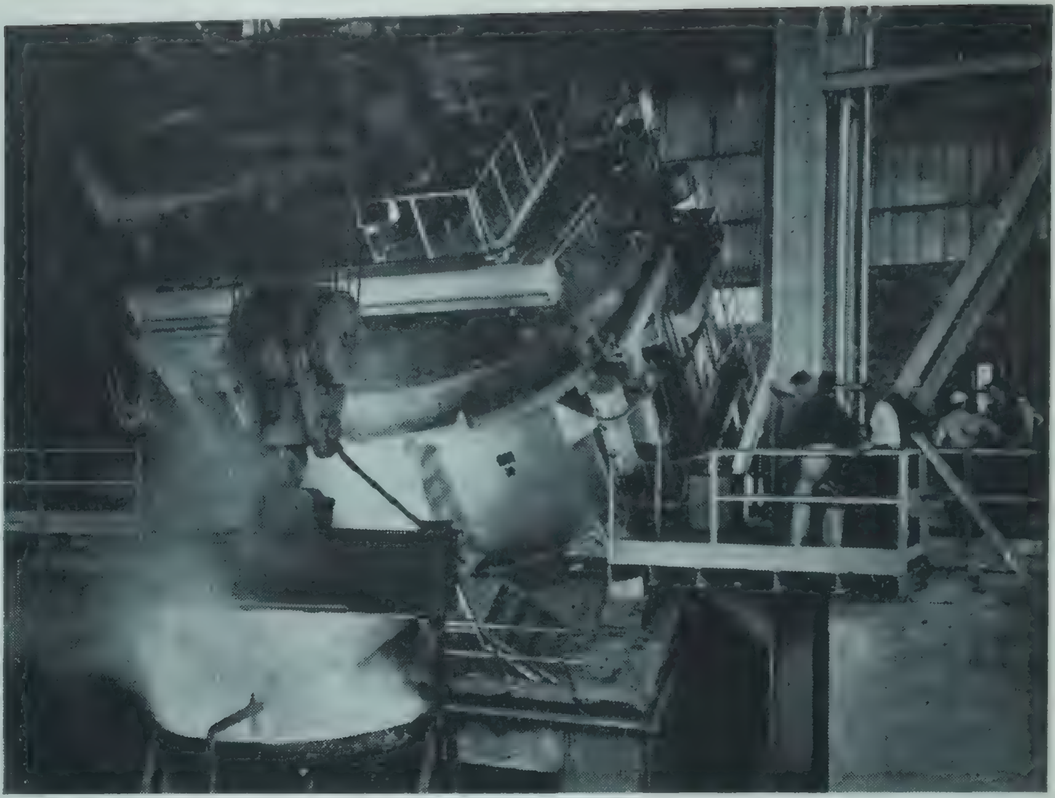
In the steam-jacketed mixers, cycles are controlled by automatic timers. In the coolers, temperature measurements determine when batches are ready for extrusion, and the temperature of the mix is recorded at the beginning and end of every extruder charge.

The proportion of green electrodes selected for physical testing varies from 100% on large sizes (12-inch diameter or larger) to about 5% on small sizes. On all sizes, however, each piece is inspected after each processing step. Green electrode samples, after cooling, are measured for length, diameter, roundness, and apparent density.

After baking, all pieces are inspected, and selected samples are checked for length, diameter, roundness, density, and electrical resistivity. These same tests are performed on samples after the graphitizing step, and further determinations are made for coefficient of thermal expansion and for the moduli of rupture, elasticity, and shear.

Metallurgical Operations Demand Larger and Larger Electrodes for Increased Production and New Applications

With the growing need throughout the world for special alloys, and the increasing tendency toward the production of even ordinary metals by electric furnace methods, a solid future is assured for synthetic graphite and amorphous carbon electrodes. Great Lakes Carbon Corp. has steadily pursued a policy of expansion and diversification which will enable it to keep up with developments in the graphite market, including electrolytic anodes



Giant Electric Furnace Competes with Open Hearth in Steel Production

Note three cylindrical graphite electrodes extending through furnace cover

A major expansion of facilities is currently nearing completion at the Morganton plant. When finished, the installation will have been increased by 40% in over-all capacity.

One building in the section now under construction will hold new graphitizing furnaces of a larger size. Each of these furnaces will hold more than four times as large a load of electrodes as will the furnaces now in use. Transformer capacity will be four times that now available, and current capacity will be doubled. In addition, there will be a decided increase in the efficiency of utilization of the power. The new furnaces are intended to satisfy the growing demand for larger diameter and longer electrodes. They will handle electrodes up to 110 inches long and 30 inches in diameter, as well as the smaller sizes now being made. The principle of operation will remain unchanged.

An interesting feature in the construction of the new power system is the aluminum bus line, which will be of welded construction rather than bolted. Each bus bar in the system will thus be a single piece, 240 feet long; all downcomers and angles are being welded. Copper bus bars are used in the original plant. When the installation was built during World War II, copper was scarce and bus bars were made of solid silver. When copper again became available, the silver was returned to the Government.

Future outlets that now appear to offer great promise for synthetic graphite manufacturers are in the production of zirconium, titanium, special alloys, and the fluorocarbons. Jet aircraft applications and atomic energy uses may also require sizable quantities of graphite as a material of construction. In connection with proposals for generation of electric power from nuclear energy, graphite is specified in several of the suggested designs, since it provides a desirable combination of nuclear and mechanical properties, and is available in the quantities required. In this application, graphite of high purity and high density is required, in order to assure maximum neutron utilization. One estimate for the construction of a 350-megawatt (heat) level power reactor, helium-cooled and graphite-moderated, indicates that nearly 1500 tons of graphite would be required for the reactor core assembly and reflector. Of this amount, approximately 1000 tons of high-grade graphite would be used in the reactor core, and another 500 tons of a perhaps slightly lower grade carbon in the surrounding reflector section.

In the metallurgical field, the output of ordinary steel by electric furnace methods is increasing at a rate twice that of the production of all steel. Here again, the trend is toward the use of larger diameter and longer electrodes, which will require further development to ensure the retention of maximum strength and proper physical characteristics as size is increased.

Research in the synthetic graphite industry is currently aimed in three directions: improvement of raw materials, improvement of basic production techniques, and development of basically different forms of graphite as well as new and different articles prepared from graphite. A typical product of this attempt to extend the diversity of the material's application is a new graphite that resists oxidation at temperatures up to 800° C. The exceptional oxidation resistance is achieved through the addition of various phosphate materials.

The past decade has witnessed widespread diversification of synthetic graphite products and has demonstrated the firm foundation upon which this industry fits into our over-all economy. It is reasonable to expect that this industry will show in the next decade at least a similar, and in all probability a greater, growth in diversity of application and improvement in process technology.

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(5) Kubaschewski, O., and Evans, E. Ll., "Metallurgical Thermochemistry," pp. 217–309, New York, Academic Press, 1951.
(6) Mantell, C. L., "Industrial Carbon," 2nd ed., New York, D. Van Nostrand Co., Inc., 1947.
(7) Ueda, Yuji, "Carbon Products," Tokyo, 1950.

Processing Equipment

(1E) Jeffery Mfg. Co., Columbus, Ohio, swing hammer pulverizers, 20–50 hp., adjustable grate bar spacings, $^1/_8$ to 1 inch.
(2E) Koehring Co., Milwaukee, Wis., rotary mix coolers, 28 cu. ft. capacity, 7.5 hp., 7.5 r.p.m., 10,300 cu. ft./min. air volume.
(3E) Ohio Machine & Boiler Co., Cleveland, Ohio, horizontal mixers, 3 ft. inside diam., rotating paddles, 15 hp., 68.5 r.p.m.
(4E) Orville Simpson Co., Cincinnati, Ohio, five-deck gyratory "Rotex" screens, screen size, 40 × 120 inches, 5 hp. drive.
(5E) Raymond Div., Combustion Engineering, Inc., Chicago, Ill., ring-roller suction mill with bag filter, 75 hp. drive, 1160 r.p.m., 60 hp. fan
(6E) Sturtevant Mill Co., Boston, Mass., vertical rotor crushers, 20 hp.
(7E) Watson-Stillman Co., Roselle, N. J., horizontal hydraulic extrusion press, tilting type, with steam-heated cylinder, ram diam. 36 inches, stroke 98 inches, ram speed 27 inches/min at full load

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Vitamin B_{12} Feed Supplement

ALBERT S. HESTER
Assistant Editor

in collaboration with

GEORGE E. WARD
Dawe's Laboratories, Inc., Newaygo, Mich.

SINCE the discovery of vitamin B_{12} in 1948, production of this vitamin has become one of the important fermentation industries in the United States. First isolated from liver, vitamin B_{12} is now obtained almost exclusively from microbial sources, either as a primary fermentation product or simultaneously with certain antibiotics. Highly purified preparations are used in the treatment of pernicious anemia and nutritional deficiencies in humans, but at the present time the most promising market for vitamin B_{12} appears to be in animal feeds. Shortly after its discovery it was found to be related to the long-sought animal protein factor (*12*) which must be added to chick diets whose protein content is solely of plant origin. The value of B_{12} in feeding weanling pigs was established (*10*), and it is now finding general acceptance as a feed supplement for both swine and poultry.

Total vitamin B_{12} production in the United States for 1952 was 94 pounds (*21*). At first glance this output might seem insignificant, but value of sales was $5,559,000. The high activity of the substance is remarkable; the amount added to a ton of feed is only a few milligrams. The price of USP crystalline vitamin B_{12} is now 29.5 cents per mg. and oral grade solids, 22.5 cents. Feed grade vitamin, which does not require complicated purification processes, is sold at a lower price.

Vitamin B_{12} Was Known by Its Effects Long Before It Was Isolated

Since 1926 liver preparations have been used in the treatment of pernicious anemia (*11*). Lack of a suitable assay for the active factor rendered isolation difficult. The only method of determining the activity of an extract sample was by clinical testing which was not practicable for isolation experiments. In 1947 it was found that certain clinically highly active fractions were microbiologically active against *Lactobacillus lactis* Dorner (*15*). Using the response of LLD as an assay procedure, small amounts of what turned out to be crystalline vitamin B_{12} were isolated almost simultaneously in this country (*13*) and in England (*17*) in 1948. Microgram quantities of the red crystalline compound produced positive hematological responses in initial tests in patients with Addisonian pernicious anemia (*22*).

Structure Is Complex and Not Yet Elucidated

Cuthbertson has given a brief review of current knowledge of the chemistry of vitamin B_{12} (*2*). It is a complex compound of the formula $C_{61-64}H_{86-92}N_{14}O_{13}PCo$; the structural formula has not yet been determined. The molecule consists of a large cobalt-containing moiety, termed cobalamine, and a cyano group coordinated with the cobalt atom. Replacement of the cyano group results in other compounds, aquocobalamin (B_{12}b), nitritocobalamin (B_{12}c), thiocyanatocobalamin, and sulfatocobalamin.

Looking for a raw material cheaper than liver, investigators found vitamin B_{12} present in several microorganisms (*14*); the possibility that the vitamin would find extensive use in human and animal nutrition stimulated a wide search for strains which could be used as commercial sources of the growth factor. Hall and his coworkers at the Northern Regional Research Laboratory screened over 5000 strains of molds, yeasts, actinomycetes, and bacteria (*5*). While there were many actinomycetes and bacteria that produced B_{12}, no satisfactory molds or yeasts were found. The NRRL workers chose *Streptomyces olivaceus* as the most promising organism and used it to develop a commercial process which was made available for licensing to industry (*6*). It is this process that Dawe's Laboratories, Inc., has used in setting up its B_{12} manufacturing operation.

There Are a Number of Commercial Processes

The principal producers of vitamin B_{12} in this country are: Commercial Solvents Corp., Dawe's Laboratories, Inc., Lederle Laboratories, Division of American Cyanamid Co., Merck & Co., Inc., Pabst Laboratories, Pacific Yeast Products, Inc., Chas. Pfizer & Co., Inc., U. S. Industrial Chemicals Co., Division of National Distillers' Products Corp., and Grain Processing Corp. Several companies are carrying out research with the idea of possibly going into vitamin B_{12} manufacturing in the future, while some of the earlier producers have dropped out of the picture.

A number of rather varied processes have been developed, both in the Department of Agriculture laboratories and by the companies themselves. Lederle produces vitamin B_{12} simultaneously with Aureomycin (chlorotetracycline) using *S. aureo-*

Culture of *Streptomyces olivaceus* in Early Stages of Development

Mycelium is generally branched and free of granulation

Five-Day Growth of *Streptomyces olivaceus* on Surface of Agar Medium

faciens. Pabst uses a process developed by themselves at their plant at Peoria, Ill. Pacific Yeast Products at Wasco, Calif., employs a primary bacterial fermentation and uses molasses as a source of carbohydrates; the bacterial cells are harvested and drum-dried. U. S. Industrial Chemicals uses an anaerobic process (*7*).

A potential source of vitamin B_{12} is sewage sludge (*8*). At the present time a Chicago engineering firm, is making a pilot plant study of the feasibility of extracting vitamin B_{12} from Milorganite (*1*), the dried sewage sludge product sold by the Milwaukee Sewage Commission. This process is not yet commercially proved.

Dawe's Laboratories Set Up Fermentation Plant at Newaygo, Mich.

The predecessor company of Dawe's Laboratories, Inc., was established in 1927 to manufacture an animal feed supplement based on milk. As nutrition knowledge advanced, the organization inaugurated production of a number of vitamins by synthesis, by extraction from fish oils, and by fermentation. The various growth factors and vitamins are blended into formulations ready for use by feed manufacturers at the company's Peoria, Ill., and Auburn, Wash., plants.

In 1949 the Dawe's organization made the decision to establish its own fermentation plant to manufacture vitamins and antibiotics for use in animal nutrition. A subsidiary company, Fermentation Products, Inc., was organized and established at Newaygo, Mich., because of favorable factors relating to water supply, suitable building, labor, and shipping. Equipment suitable for producing a variety of different fermentation end products was selected, and erection of the working units was begun in the summer of 1950.

The processes chosen for initial operation at the new plant were those developed by the Fermentation Division of the Northern Regional Research Laboratory, Peoria, Ill., for the production of riboflavin and vitamin B_{12}, and actual production of these vitamins at Newaygo was started in the fall of 1950 under license from the U. S. Department of Agriculture (*3, 19*). Comprehensive laboratory and pilot plant data provided by the Fermentation Division and Engineering and Development Division of the Northern Regional Research Laboratory made possible large scale production with minimum delay.

The organism used for vitamin B_{12} production is *S. olivaceus* NRRL B-1125. Stock cultures are carried on slants of Bennett's agar (*9*). The slants are incubated at 28° C. for 4 to 6 days until they are sporulated; these stock cultures may then be used directly or stored in the refrigerator for several weeks and used as needed.

Spores are transferred from slants to 1-liter Erlenmeyer flasks containing 250 ml. of medium; the composition of the medium, which is the same as that used in the fermentors, is shown in Table I. The flasks are incubated at 28° C. on a rotary shaker (*6E*) for about 48 hours and are then used to inoculate 3-liter flasks containing 1500 ml. of medium. These flasks are incubated on a reciprocal shaker. When growth is sufficient the 3-liter flasks are used to inoculate seed fermentors (Figure 1). A glass inoculating bell attached to a side arm of the flask by a rubber tube provides the means of making an aseptic transfer to the seed fermentor.

Table I. Typical Medium Composition

Distillers' solubles, %	4.0
Dextrose, %	0.5-1.0
$CaCO_3$, %	0.5
$CoCl_2.6H_2O$, p.p.m.	1.5-10

Various alternative methods may be employed for developing inoculum. One possible variation is to eliminate the second flask step entirely and use five or six of the smaller flasks to inoculate a seed fermentor. Another variation involves development of an inoculum by bubbling sterile air through several liters of medium in a glass bottle; such medium may be inoculated with spores or with a vegetative growth of *S. olivaceus*. The air may pass into the medium through an open tube or through a sparger device.

Fermentation Takes Place in 5200-Gallon Fermentors

The seed fermentors are 400-gallon vessels (*5E, 7E*) in which 220 to 260 gallons of inoculum are developed for the production

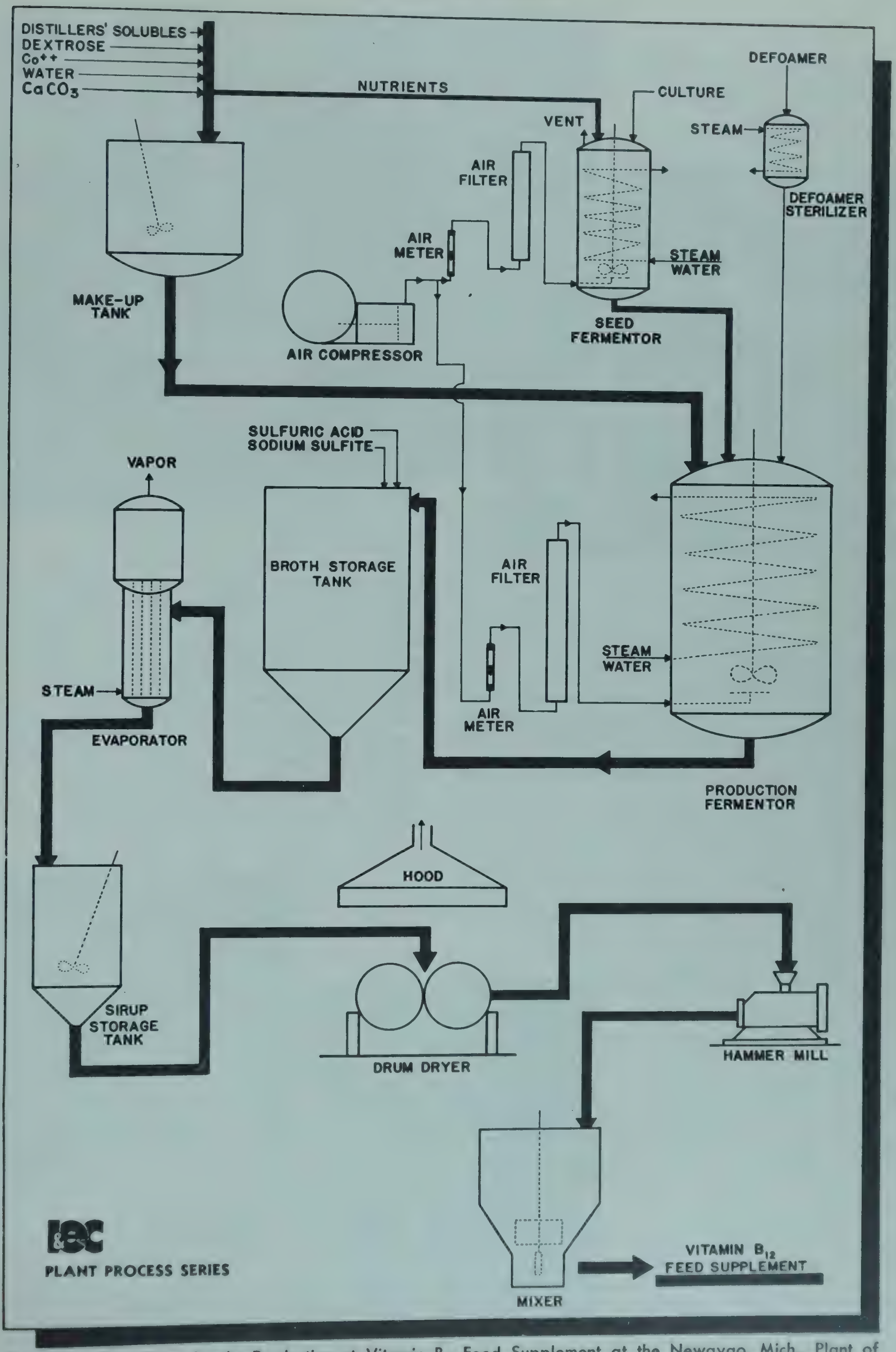
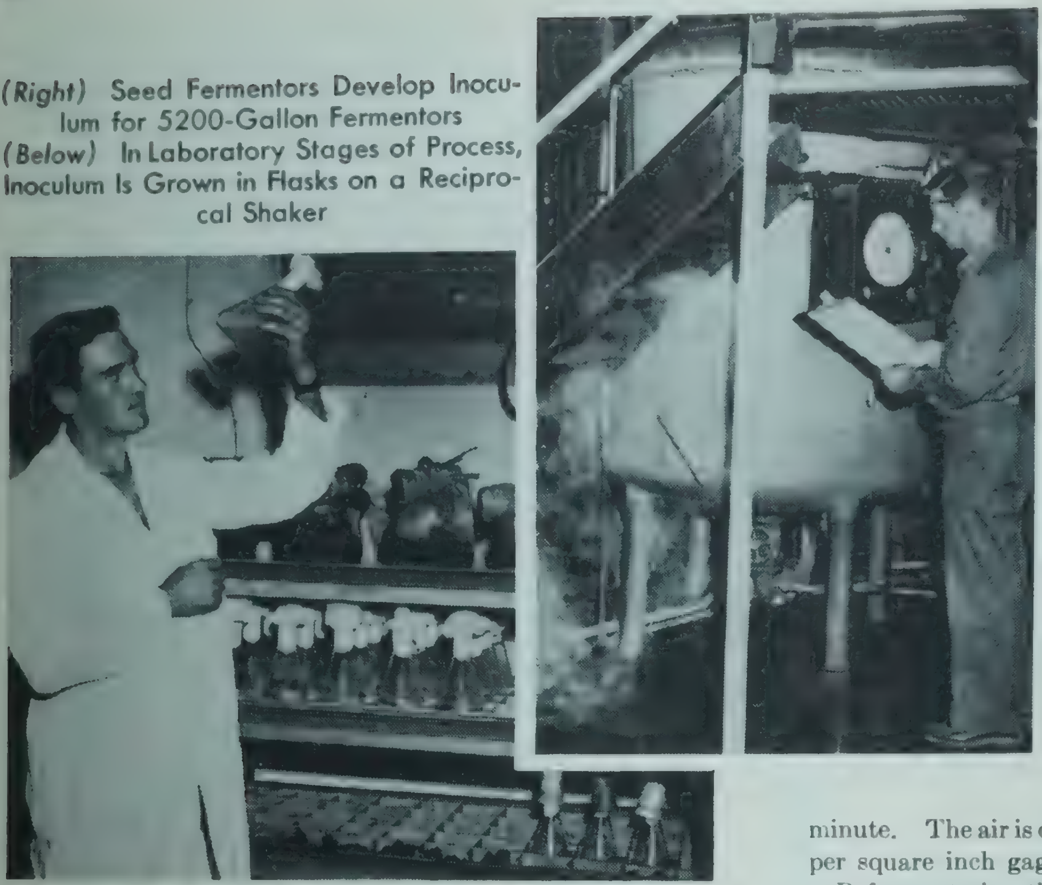

DISTILLERS' SOLUBLES
DEXTROSE
Co^{++}
WATER
$CaCO_3$
NUTRIENTS
CULTURE
DEFOAMER
VENT
STEAM
AIR FILTER
DEFOAMER STERILIZER
AIR METER
STEAM WATER
MAKE-UP TANK
AIR COMPRESSOR
SEED FERMENTOR
SULFURIC ACID
SODIUM SULFITE
VAPOR
BROTH STORAGE TANK
AIR FILTER
STEAM WATER
STEAM
EVAPORATOR
AIR METER
PRODUCTION FERMENTOR
HOOD
SIRUP STORAGE TANK
DRUM DRYER
HAMMER MILL
I&EC
PLANT PROCESS SERIES
MIXER
VITAMIN B_{12} FEED SUPPLEMENT

Figure 1. Flow Sheet for the Production of Vitamin B_{12} Feed Supplement at the Newaygo, Mich., Plant of Dawe's Laboratories, Inc.

(Right) Seed Fermentors Develop Inoculum for 5200-Gallon Fermentors
(Below) In Laboratory Stages of Process, Inoculum Is Grown in Flasks on a Reciprocal Shaker



fermentors, which are 5200-gallon tanks (*5E, 7E*). The seed and production fermentors are similar in construction. They are mild-steel pressure vessels equipped with coils for steam or cooling water, agitators, and air spargers.

The dry nutrients for the seed tanks are placed directly into the fermentor, and the batch is made up to volume with water. Ingredients for the production fermentors are placed in a 1000-gallon, conical-bottomed open-top make-up tank. Water is added, and the mixture is agitated by inclined agitators; pH is adjusted to 6.5 to 7.0 with caustic soda. The slurry is then pumped through a header and hose into a selected fermentor; rinse water serves to purge the lines and bring the mash to the desired volume.

The manhole of the seed tank or fermentor is closed, and the nutrient medium therein is sterilized at 121° C. for an hour. Steam is passed through the coils and is also blown into the tank through every available opening—the air intake, the inoculum line, the bottom outlet. and the sample line. The agitator is kept on during sterilization. About 60 minutes is required for the sterilization temperature to be reached, and another 60 to 90 minutes is needed to cool the medium to 28° C., the fermentation temperature

The seed tanks are inoculated from the laboratory culture through a short piping connection provided for that purpose at the top of the tanks. When not in use the inoculum connection is closed off from the fermentor by a valve, and a steam seal is maintained against the outer side of this valve. The several seed fermentors are connected to a manifold leading to the several large fermentors. thereby permitting the inoculum from any one of the seed tanks to be admitted to any large fermentor. This arrangement gives maximum plant flexibility and avoids delays in starting fermentors in case inoculum tanks might be unsuitable for use at a scheduled time All pipelines between the seed fermentors and the large fermentors are maintained under steam pressure except when in use in order to prevent contamination

During fermentation, the temperature of the medium is maintained at 28° C by the admission of steam or cooling water into the coils of the fermentors; such admission is controlled by automatic recorder-controllers (*11E*). Sterile air is admitted through the spargers at ratio of 0.1 to 0.5 volume per volume of medium per minute, and the agitators are usually operated during the entire fermentation period

Foaming of the aerated medium presents problems, particularly at the beginning and the end of the fermentation period. The addition of oils, such as corn oil, soybean oil, and lard oil, to the medium before cooking helps to control foaming, and it sometimes is desirable to add more sterile oil during the fermentation. Thirty-gallon pots, in which oil may be heated with steam at 125° to 150° C. to sterilize, are connected with the individual production fermentors.

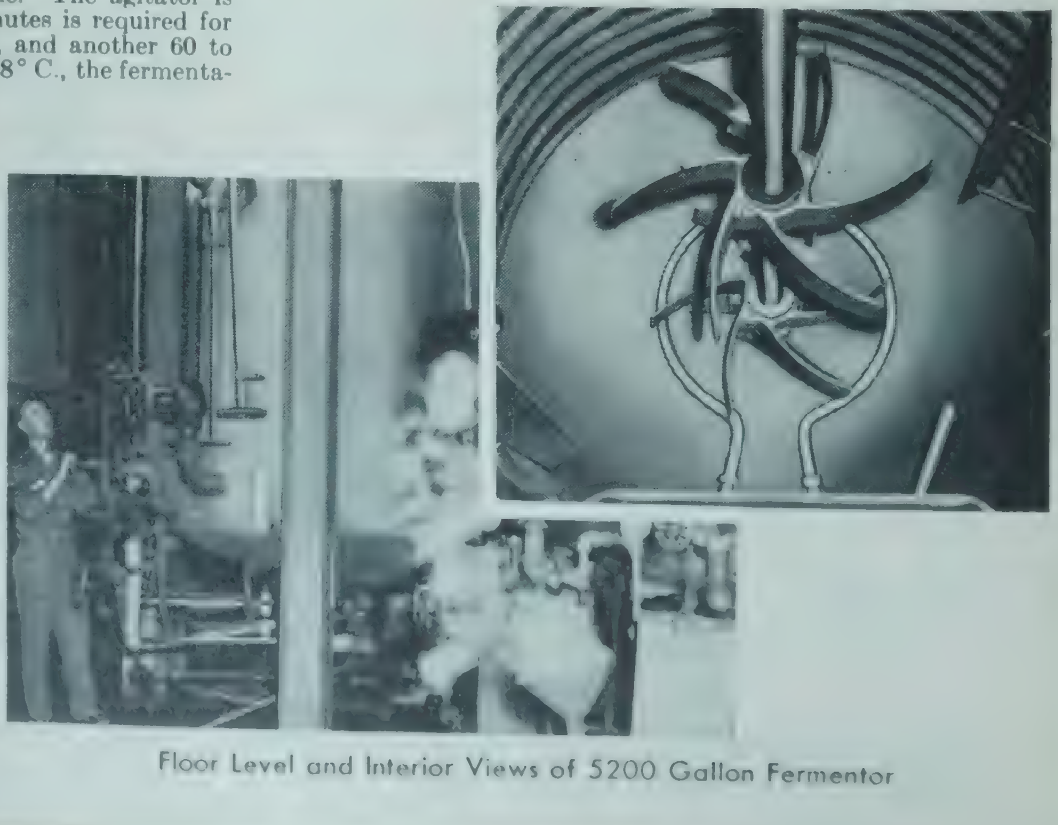
Air Sterilization Is Important Phase of Aerobic Fermentation

Air for aeration of the fermentors is provided by three horizontal single-stage compressors (*2E*) rated to deliver 540 cubic feet per minute and by one Y-type double-acting compressor (*3E*), rated to deliver 850 cubic feet per minute. The air is discharged from the compressors at 35 pounds per square inch gage.

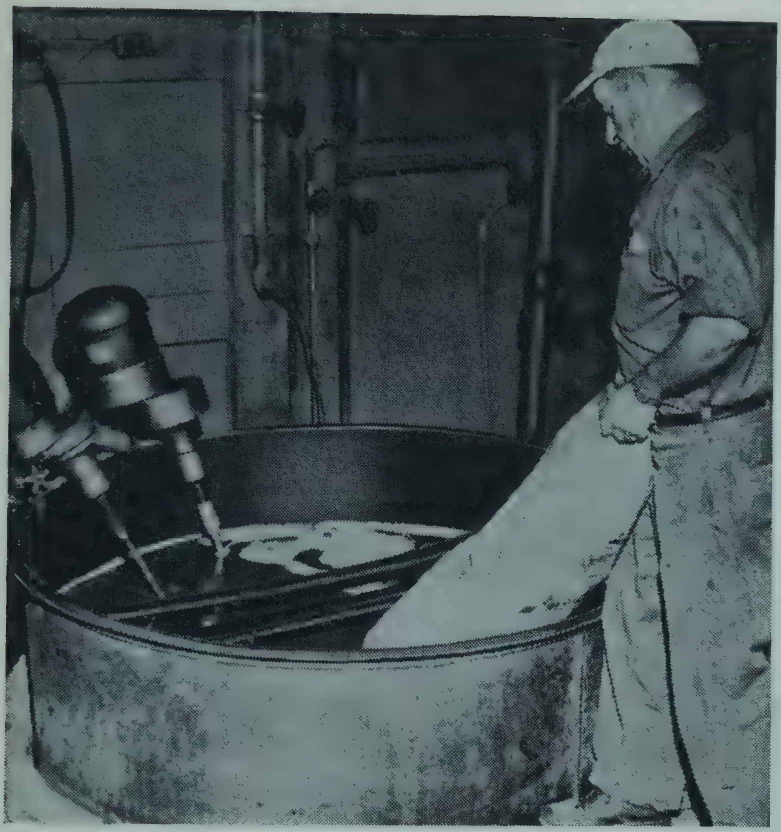
Before entering the seed fermentors or the production fermentors the air is sterilized by passage through a bed of granular activated carbon. Each fermentor has its own carbon filter, which is sterilized with steam during the time the fermentation medium is being sterilized. Steam is blown downward through the carbon to flush out any foreign material; air is passed upward. The steel cylinders that hold the carbon for the seed fermentors are 8 feet high and 10 inches in diameter, and the ones used for the production fermentors are 8 feet high and 18 inches in diameter.

The flow of air to seed tanks and production fermentors is measured by rotameters (*4E*) installed upstream from the air filters.

The culture is grown in the seed tanks for 2 days. Before any seed tank is used to inoculate a production fermentor, it



Floor Level and Interior Views of 5200 Gallon Fermentor



Make-up Tank for Mixing Nutrients for Large Fermentors

is carefully examined by microscope and by bacteriological tests to ensure that a healthy, uncontaminated culture of *S. olivaceus* has developed.

The production fermentors are operated for 3 to 5 days. About 24 hours after inoculation the production mash becomes very thick. This results not only from the mycelial growth of the organism but probably also from the formation of viscous substances such as polysaccharides. After the available nutrients in the medium have been exhausted, lysis of the mycelium takes place, the pH rises to 8.0 or above, and the mash becomes quite thin. The fermentors are usually harvested about this time, since no more B_{12} is formed after lysis starts. The vitamin B_{12} content of the broth at the end of fermentation is usually within the range 1.0 to 2.0 micrograms per ml. of broth (Figure 2).

When fermentation is completed the mash is pumped into storage tanks, and the vitamin B_{12} is stabilized by reducing the pH to 5 with sulfuric acid and adding a small quantity of sodium sulfite.

Fermented Broth Concentrated by Evaporation, Then Dried

Total solids, which amount to only about 3% in the fermented mash, are increased to 15 to 20% by evaporation in vacuo in a long-tube vertical evaporator (*10E*) or in a vacuum pan (*9E*). The resulting sirup is then fed to a steam-heated atmospheric double-drum dryer (*8E*) which yields a solid product containing only about 5% moisture. Suitable storage tanks for the sirup are provided between the evaporators and the dryer.

Batches of dried material weighing from 3000 to 4000 pounds are passed through a hammer mill (*12E*) and thence to a mixer (*1E*) from which the product, made uniform with respect to particle size and potency, is drawn off into bags or fiber drums, ready for shipment. The vitamin B_{12} content of the finished product ranges from 10 to 30 mg. per pound, as determined by the USP and AOAC methods of microbiological assay using *Lactobacillus leichmannii* (*16*). This potency has also been confirmed by numerous nutritional tests.

The final product contains desirable nutritional factors in addition to vitamin B_{12}. The protein content is about 35%, and the presence of appreciable quantities of niacin, pantothenic acid, pyridoxin, thiamin, and riboflavin has been reported by NRRL workers (*4*), who also detected antibiotic substances in *S. olivaceus* broths.

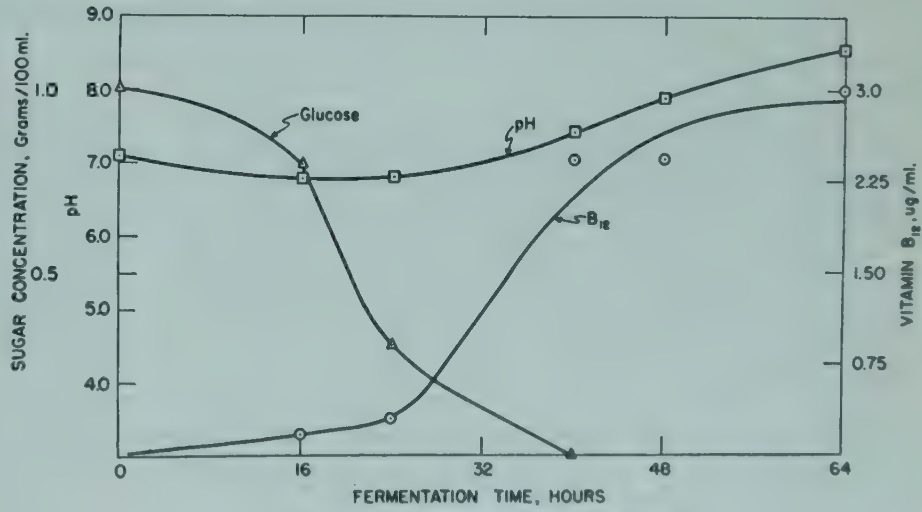
Newaygo Plant Also Produces Riboflavin

Riboflavin production at the Newaygo plant is conducted in a manner essentially similar to that just described for vitamin B_{12}, except that the medium constituents are different, and the organism employed is *Ashbya gossypii*, a yeastlike fungus. The riboflavin mash is composed of dextrose, corn steep water, and animal stick liquor, as described by Tanner *et al.* (*18*) of the Northern Regional Research Laboratory, and the whole mash is dried, after fermentation, to yield a product containing protein, riboflavin, and other valuable nutritional factors.

Laboratory Control

Control and improvement of the fermentation processes operated at the Newaygo plant are considered important and essential. A research and development group of chemists and bacteriologists studies the strains of microorganisms used in the plant processes and searches for strains that have superior vitamin-producing ability, grow more prolifically, or produce seed (spores) more easily and uniformly. Physical conditions in the plant fermentors are also studied with a view toward improvements in operation. Raw materials used in the plant are tested for suitability in the processes, and potential new raw materials offering technical or economic advantages are investigated.

An operations control laboratory schedules and supervises the development of the production cultures in the laboratory stages and also the starting and harvesting of seed tanks and production fermentors. Samples taken from all fermentation vessels daily or oftener are tested to determine pH and reducing sugar content, and aseptic samples are examined by microscope and by subculturing into broth designed to show the presence of bacterial contaminants. The pH measurements are particularly helpful as one indication of normal or abnormal behavior.



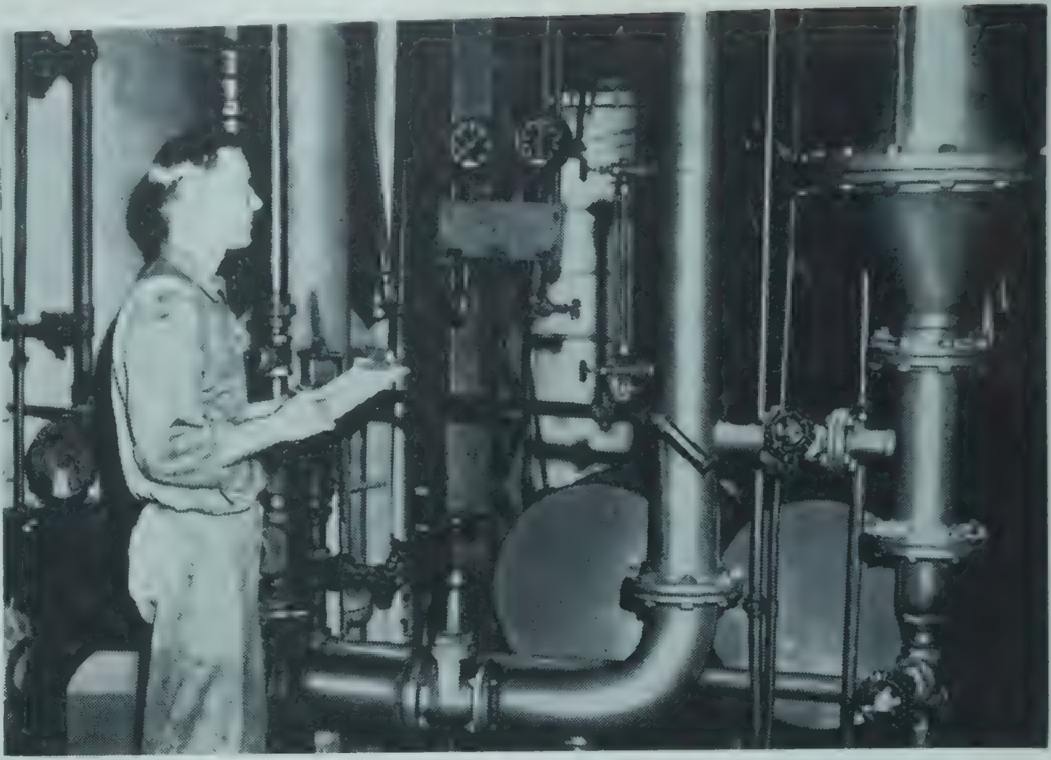
CHANGE IN MEDIUM DURING FERMENTATION

Figure 2

Courtesy *Applied Microbiology* (*4*)

Bacterial contamination of fermentors producing either vitamin B_{12} or riboflavin usually lowers the yield of these desired products, and it is very important to operate the equipment so as to avoid contamination and to have means to detect contamination when it occurs. Elimination of contamination has been found to require (*a*) thorough sterilization of the mash during cooking; (*b*) protection by steam seals of all valves opening into fermentors; and (*c*) complete sterilization of the air used for aeration of the mash.

The Dawe's operation at Newaygo also includes an assay laboratory that analyzes for riboflavin by the fluorometric method and for vitamin B_{12} by the USP or AOAC microbiological method, using *L. leichmannii* ATCC 4797 as the test organism. Assay control is imposed throughout the entire process, including the fermentation broths, the concentrated sirups, the drum-dried material, the blended Newaygo products, and finally the commercial blends produced at the Peoria and Auburn plants of the company.



Lower Level of Swenson Evaporator

Outlook for Feed Supplements Is Good

There is every indication that sales of vitamin B_{12} feed supplements should continue to increase. More and more feed manufacturers are realizing their value in swine and poultry feeds. The decrease in sales from $11,044,000 in 1951 (*20*) to $5,599,000 in 1952 (*21*) did not reflect lessened production, but a lower price; production was 84 pounds in 1951, 94 pounds in 1952. This is the normal situation which might be expected to follow the introduction of a new product; at first the price is high, then competition and improved technology raise output and bring the price down.

An interesting side light in the commercial development of vitamin B_{12} as an animal feed supplement is that it is indirectly responsible for opening a new market for antibiotics. Some of the first B_{12} used in animal nutrition experiments was prepared from antibiotic residues. It was soon found that the small quantities of antibiotic left in some of the products were themselves beneficial. Consequently in 1952, $16,962,000 worth of feed grade antibiotics was sold.

The Northern Regional Research Laboratory and others are looking for a microorganism capable of producing both vitamin B_{12} and an antibiotic suitable for use as a feed supplement. A large number of antibiotics have been found. Most of these are toxic or of unproved utility for pharmaceutical use but might nevertheless eventually prove to be as good or better than the antibiotics now on the market as far as feed uses are concerned. There is good reason to believe that there will be other growth factors discovered which in all likelihood can be produced most economically by microorganisms.

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(21) *Ibid.*, 1952, GPO Cl. No. TCl. **9:190** (1953).

(22) West, R., *Science*, **107**, 398 (1948).

Processing Equipment

(1E) Brower Mfg. Co., Quincy, Ill., below-floor model mixer, 4000 lb., Model 49-4935V.

(2E) Chicago Pneumatic Tool Co., New York, N. Y., horizontal single-stage compressor, 75 hp.

(3E) *Ibid.*, Y-type heavy-duty double-acting compressor, 100 hp.

(4E) Fischer & Porter Co., Hatboro, Pa., Flowrator meters.

(5E) Graver Tank & Mfg. Co., East Chicago, Ind., custom-built mild-steel fermentor.

(6E) B. F. Gump Co., Chicago, Ill., custom-built laboratory flask shaker (rotary).

(7E) Leader Iron Works, Inc., Decatur, Ill., custom-built mild-steel fermentor.

(8E) Overton Machine Co., Dowagiac, Mich., drum dryer, Model 42A.

(9E) C. E. Rogers Co., Detroit, Mich., vacuum evaporating pan.

(10E) Swenson Evaporator Co., Div. of Whiting Corp., Harvey, Ill., custom-built long-tube vertical vacuum evaporator.

(11E) Taylor Instrument Companies, Rochester, N. Y., air-operated recorder-controller.

(12E) W-W Grinder Co., Wichita, Kan., hammer mill.

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Pyrethrum Flowers

In Production of Ethyl Diazoacetate, Operators Perform All Operations from Behind a 14-Inch Reinforced Concrete Barricade

HOWARD J. SANDERS, *Associate Editor*
in collaboration with
ALBERT W. TAFF
U. S. Industrial Chemicals Co., a Division of National Distillers Products Corp., Baltimore, Md.

ALLETHRIN

ON MARCH 11, 1949, a leading spokesman for the U. S. Department of Agriculture's Bureau of Entomology and Plant Quarantine formally announced a major achievement in the field of insecticidal research. To representatives of the press, he reported that three USDA chemists had successfully carried out the first total synthesis of not only one of the most complex but also one of the most valuable insecticides ever developed. Working at the USDA laboratory in Beltsville, Md., LaForge, Schechter, and Green had performed the first total synthesis of a pyrethrin-type ester, later named allethrin.

This achievement was promptly heralded in scores of trade and technical journals throughout the world. The synthesis of allethrin was acclaimed as a major milestone in the field of chemical research—comparable in importance to the development of synthetic rubber.

This relatively new insecticide is the allyl homolog of cinerin I. The chief chemical difference between allethrin and cinerin I, apart from stereochemical considerations, is that in allethrin the 2-butenyl group is replaced by an allyl side chain. Cinerin I, in turn, is one of the four active components isolated thus far from the natural insecticide, pyrethrum.

Since the beginning, the history of allethrin has been intimately associated with that of pyrethrum. Allethrin, in fact, was especially developed as a means of supplementing the world's limited supply of pyrethrum. This latter insecticide is obtained from pyrethrum flowers, which, similar in appearance to daisies, are members of the chrysanthemum family. Approximately 1.0 to 1.5% by weight of dried pyrethrum flowers is recovered as the effective insecticide (*2*).

The use of pyrethrum in Europe began in the early 1800's. The commercial history of pyrethrum, however, dates back only to about 1918, when a kerosine extract of pyrethrum flowers was found to be highly potent as a spray against flies, mosquitoes, and other insects. Pyrethrum, it was discovered, not only gives quick knockdown and kill but, in normal use, is completely free of toxicity to man and animals (*27*). It is, therefore, quite safe for household application and for use on foods, grains, animals, and on field crops immediately before harvest.

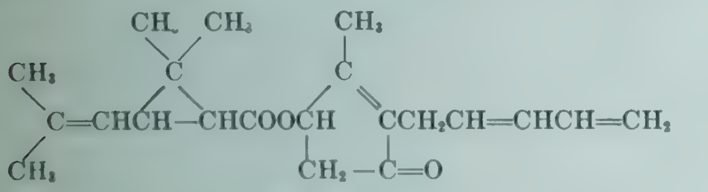
Despite these compelling advantages, pyrethrum suffers from several major handicaps, not the least of which is its limited, unstable supply. The economical cultivation of pyrethrum flowers requires a highly favorable combination of climate, soil, elevation, land cost, and labor cost—conditions that are found in very few parts of the world. In general, pyrethrum flowers can only be grown on a commercial scale at high altitudes near the equator. Such countries as Kenya, Belgian Congo, and Brazil are today among the world's leading suppliers.

To reach American markets, pyrethrum flowers must be transported over vast distances, a factor which not only adds to their cost but which ordinarily renders the pyrethrum supply extremely uncertain in time of war. Subject to the vagaries of weather and to numerous other factors, pyrethrum lacks the basic dependability essential to the continued increasing use of a major insecticide.

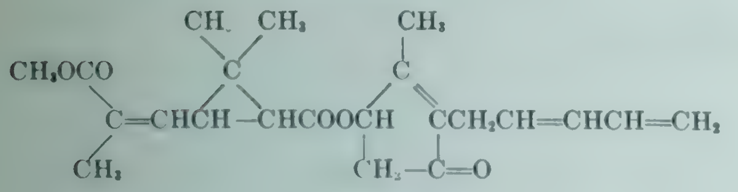
Efforts Made to Develop Synthetic Insecticide Having Same Desirable Properties as Pyrethrum

For many years, these problems, clearly reflected in the wide swings in the price of pyrethrum, gave increasing impetus to the search for new compounds equally as effective in killing insects and, at the same time, just as harmless to man and animals. What was needed was an entirely synthetic insecticide that could be produced in the United States in unlimited quantities from freely available raw materials.

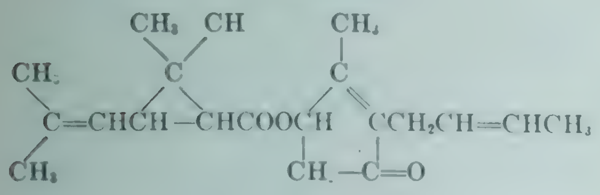
As one method of attack, researchers attempted to determine the exact chemical components that render pyrethrum toxic to insects. Actually, this work had been going on for years. In 1924, Staudinger and Ruzicka in Switzerland had made important contributions to the field by determining the acid segments of two of pyrethrum's insecticidal components, pyrethrins I and II (*26*). Furthermore, they made considerable progress in determining the pyrethrolone segments of pyrethrins I and II. The full solution to this problem, however, required years of additional work, mainly by LaForge and coworkers at the Department of Agriculture. In the course of their studies, LaForge and collaborators discovered two additional active principles of the insecticide, namely cinerins I and II. Then in 1947, LaForge and coworkers reached one of their major goals by achieving the final determination of the structures of pyrethrins I and II and cinerins I and II (*16*).



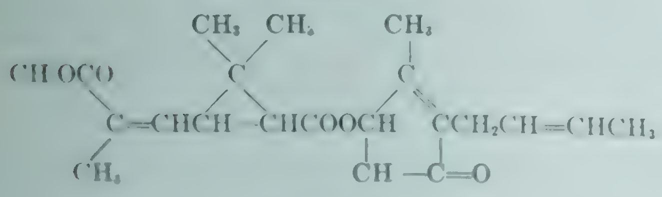
Pyrethrin I



Pyrethrin II



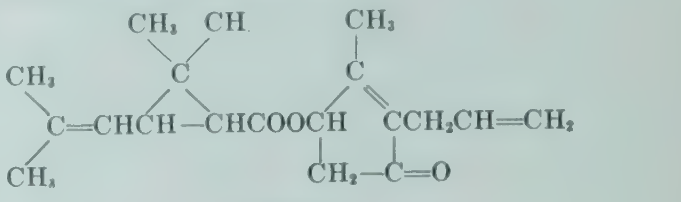
Cinerin I



Cinerin II

Early in 1948, research at the USDA laboratory was directed toward the total synthesis of cinerin I, mainly because this compound, of all the four active materials isolated from pyrethrum, is the simplest chemically and the most stable. By then, Campbell and Harper in England had already announced an improved synthesis of chrysanthemum monocarboxylic acid (*1*), an important intermediate in the synthesis of cinerin I. The remaining problem was to prepare the ketoalcoholic segment of the molecule (*20*).

After months of work, Schechter, LaForge, and Green developed a general synthesis of cyclopentenolones (*21, 25*), which removed the last barrier to the preparation of cinerin I. Having accomplished this, the USDA chemists began testing a wide variety of compounds related to cinerin I, in an effort to discover a compound possessing possibly even greater insecticidal value than cinerin I itself. Of the compounds tested, the most potent and also the most suitable for commercial development was the allyl homolog of cinerin I, or allethrin (*16*).



Allethrin

The Government's extensive research program on this insecticide led to a number of basic allethrin patents (*22–24*), which are available for the free use of all persons in the United States. Since the Government had no interest in the foreign development of allethrin, U. S. Industrial Chemicals Co. early in 1950 acquired all foreign rights to these patents (*3*). Although no licenses have yet been granted for the production of allethrin abroad, several are in the process of negotiation. Manufacture in one or more foreign countries is a possibility in 1955.

The name "allethrin," which was adopted by the Department of Agriculture's Interdepartmental Committee on Pest Control early in 1950, was announced in March of that year at a meeting at Boyce Thompson Institute in Yonkers, N. Y. (*17*). At the same meeting, Carbide and Carbon Chemicals Co. reported the first commercial synthesis of allethrin, which up until that time had been known as allyl cinerin in this country and as allylrethrin in England.

Allethrin, an Oily Liquid, Consists of a Mixture of Eight Optically Active Isomers

Since both cis and trans forms of *d*- and *l*-chrysanthemum monocarboxylic acid are esterified with both *d*- and *l*-allethrolone in the synthesis of allethrin, the insecticide consists of a mixture of eight optically active isomers (*19*). Each of these isomers has its characteristic insecticidal properties.

Commercial allethrin is an oily liquid that varies in color from pale yellow to reddish brown depending on the concentration of impurities. Some of the physical properties of allethrin are indicated in Table I

Table I. Physical Properties of Commercial Allethrin (*17*)

Color on Gardner scale	15 (max.)
Specific gravity at 20°/20° C.	1.005–1.015
Refractive index at 20° C.	1.5010
Refractive index at 30° C.	1.5010–1.5035
Acidity calculated as chrysanthemum monocarboxylic acid	Less than 3%
Odor	Mild, aromatic
Freon insolubles	Less than 0.1%

Allethrin is used primarily in household and military aerosols and sprays for the control of flies and mosquitoes (*8*). Like pyrethrum, allethrin has the advantage both of quick knockdown and nontoxicity to humans and animals. Moreover, it has been found effective against insects resistant to DDT and other chlorinated insecticides.

The official acceptance of allethrin for use in gas-propelled aerosols was announced by the Department of Agriculture in

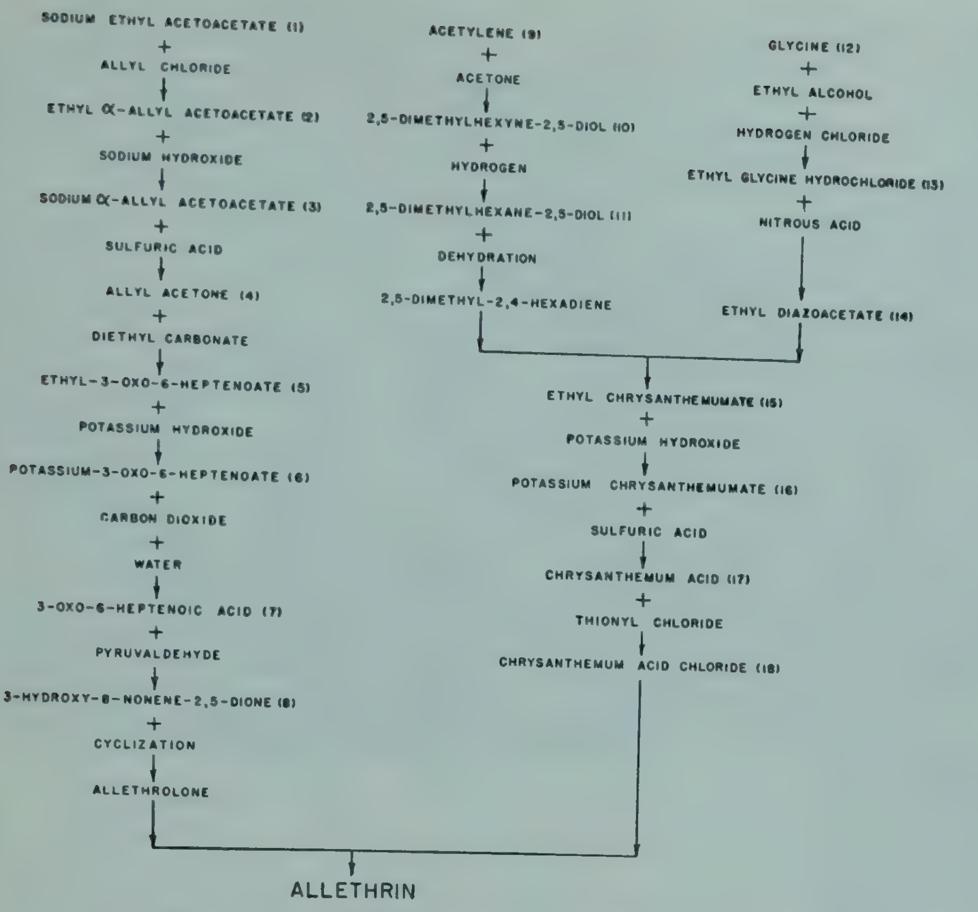

SODIUM ETHYL ACETOACETATE (1)
ALLYL CHLORIDE
ETHYL α-ALLYL ACETOACETATE (2)
SODIUM HYDROXIDE
SODIUM α-ALLYL ACETOACETATE (3)
SULFURIC ACID
ALLYL ACETONE (4)
DIETHYL CARBONATE
ETHYL-3-OXO-6-HEPTENOATE (5)
POTASSIUM HYDROXIDE
POTASSIUM-3-OXO-6-HEPTENOATE (6)
CARBON DIOXIDE
WATER
3-OXO-6-HEPTENOIC ACID (7)
PYRUVALDEHYDE
3-HYDROXY-8-NONENE-2,5-DIONE (8)
CYCLIZATION
ALLETHROLONE
ACETYLENE (9)
ACETONE
2,5-DIMETHYLHEXYNE-2,5-DIOL (10)
HYDROGEN
2,5-DIMETHYLHEXANE-2,5-DIOL (11)
DEHYDRATION
2,5-DIMETHYL-2,4-HEXADIENE
GLYCINE (12)
ETHYL ALCOHOL
HYDROGEN CHLORIDE
ETHYL GLYCINE HYDROCHLORIDE (13)
NITROUS ACID
ETHYL DIAZOACETATE (14)
ETHYL CHRYSANTHEMUMATE (15)
POTASSIUM HYDROXIDE
POTASSIUM CHRYSANTHEMUMATE (16)
SULFURIC ACID
CHRYSANTHEMUM ACID (17)
THIONYL CHLORIDE
CHRYSANTHEMUM ACID CHLORIDE (18)
ALLETHRIN

Figure 1. Material Flow Sheet for Synthesis of Allethrin

October 1950. By October of the following year, the Army had purchased more than 7,000,000 12-ounce aerosol bombs containing allethrin in place of pyrethrum (*18*). By mid-1952, more than 12,000,000 allethrin aerosol bombs of all types had been sold, and since then many millions more have been produced.

In addition to its military and household applications, allethrin is used on animals and livestock, mainly in fly control. To an increasing extent, allethrin is also being used in sprays and dusts for the protection of stored grains. Only to a very limited extent, however, is this insecticide finding application in the growing of farm crops, partly because of its high price.

In 1950, the first year of commercial production, allethrin sold for $55 a pound on a 100% basis. The current selling price on the same basis is $32 a pound. Although no immediate reduction in the price of allethrin is anticipated, future improvements in processing will inevitably lead to price cuts. In this regard, the greatest hopes for significant reductions of price lie in marked improvements in yields, the more efficient recovery of solvents and by-products, and in the development of major new uses for allethrin intermediates.

Production Involves One of the Most Complex Syntheses Ever Carried Out on Commercial Scale

The manufacture of allethrin is one of the most complex chemical syntheses ever undertaken commercially. The entire process requires from 12 to 20 separate chemical steps, depending on the availability of raw materials (*12*). In recent years, the large scale production of allethrin has been carried out successfully by Carbide and Carbon Chemicals Co., Benzol Products Co., and U. S. Industrial Chemicals Co. Through their efforts, the output of this insecticide has climbed from about 8500 pounds in 1950 (*7*) to about 50,000 pounds in 1953.

The first company to launch commercial production of allethrin was Carbide and Carbon Chemicals, which completed its first batch of this material in March 1950, just one year after the USDA announcement of the total synthesis. Since Carbide was already a manufacturer of such raw materials as pyruvaldehyde and ethyl acetoacetate, production of allethrin fitted in well with the company's existing chemical operations. In its manufacture of allethrin, Carbide used equipment already available at its South Charleston, W. Va., plant. In its necessarily lengthy and involved process, Carbide was obliged to handle no less than 200 pounds of about 25 different chemicals for the synthesis of one pound of allethrin.

In 1950, the company produced a single batch of allethrin amounting to about 5000 pounds (*5*). In 1951, it turned out a second 5000-pound batch, and a third batch of approximately the same size in 1952. This output went largely to the armed forces and to various insecticide formulators (*10*). Currently Carbide is building a $6,000,000 plant at Institute, W. Va., with capacity for 400,000 to 500,000 pounds of allethrin a year. Completion of this plant is scheduled for April 1954.

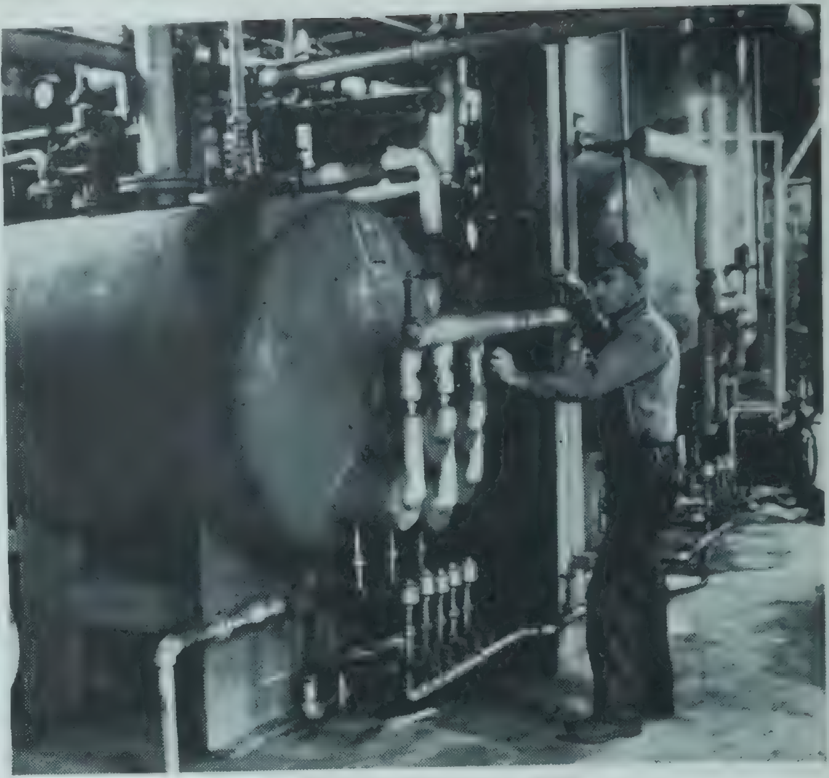
Although Carbide was the first company to manufacture allethrin commercially, the largest producer thus far has been Benzol Products, which completed its first commercial synthesis at its plant in Piscataway, N. J., in August 1950. The company's next run was made in December 1950, and production has followed continuously ever since. In 1951, the first full year of production, Benzol Products turned out about 23,000 pounds of allethrin, while its production in 1953 was about 30,000 pounds. The company's entire allethrin output is distributed by McLaughlin Gormley King.

Like Carbide, Benzol Products uses the basic USDA synthesis with a variety of process modifications. At the start, the company depended almost entirely on equipment already on hand. To keep pace with growing demand, however, Benzol Products has since appreciably enlarged its facilities. By June 1952, the company's allethrin capacity had been expanded to 100,000 pounds a year—an eightfold increase in less than 2 years (*11*).

U. S. Industrial Chemicals Developed Immediate Interest in Synthesis of the New Insecticide

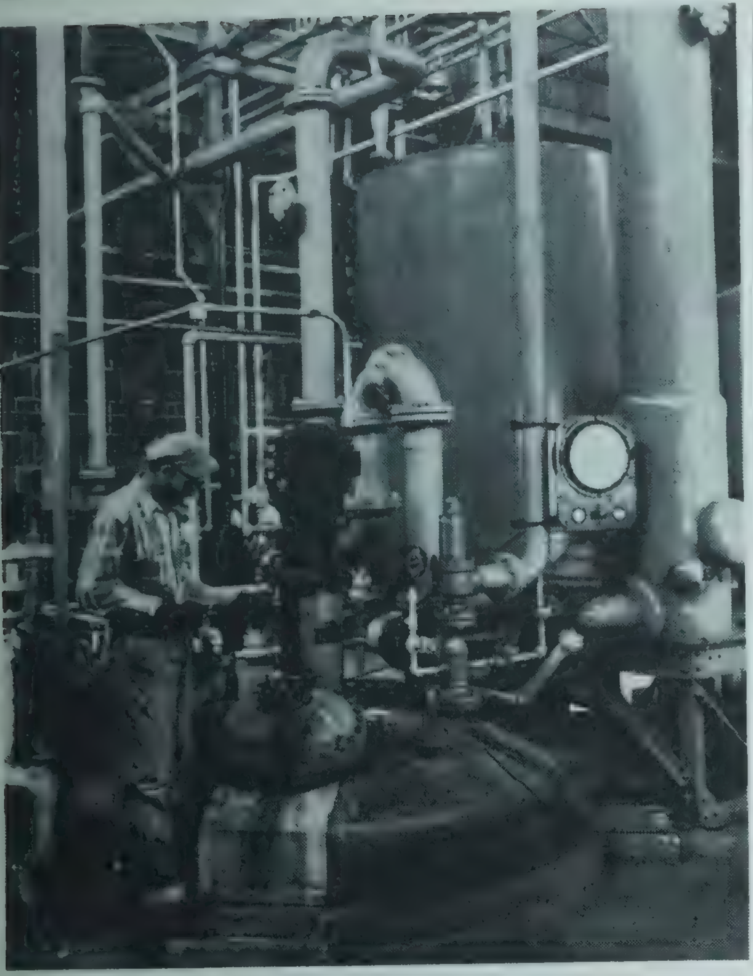
The second largest producer of allethrin today is U. S. Industrial Chemicals, a company that, besides being an important manufacturer of synthetic organic chemicals, is also the world's largest processor and distributor of pyrethrum. Within a month after the synthesis of allethrin was announced by the Department of Agriculture, a sample of the compound was prepared by the Schechter-LaForge method in the USI laboratories. It soon became evident, however, that the USDA synthesis, no matter how elegant, could not readily be adapted in all respects to the demands of large scale production. New procedures had to be developed to increase yields, simplify techniques, and to side-step hazardous reactions (*27*).

USI spent fully 2 years in research and development, both in the laboratory and pilot plant, before attempting the commercial production of allethrin. As a result, many important process changes were made. For example, one of the intermediates, 2,5-dimethyl-2,4-hexadiene, was originally produced by the isomerization of 2,5-dimethyl-1,5-hexadiene, which, in turn, was synthesized from methallyl chloride by the Grignard reaction. To replace the Grignard step, which involves the hazardous use of magnesium and ether, an entirely different series of reactions



▲ Still for Recovery of Ethyl Acetate from Reactor 1

Directly behind operator is crude allyl acetone distillation unit



◀ Operator Preparing to Take a Sample from Reactor 1

In background, Reactor 2 is at left and ethyl acetate tank at right

was developed. In another process improvement in the same phase of the allethrin synthesis, the use of calcium carbide in the preparation of 2,5-dimethylhexyne-2,5-diol was replaced by the direct use of the more convenient raw material, acetylene.

After months of pilot plant work, USI in 1951 decided to build a 75,000-pound-a-year allethrin plant in the Fairfield section of Baltimore, Md. (*6*). Construction of the new installation began in September 1951 and was completed in July 1952 at a cost of $1,300,000. Significantly, the new unit was the first fully integrated plant ever built for the manufacture of allethrin. All previous production had been carried out on a step-by-step basis in existing, necessarily unrelated equipment. In the new plant all equipment was carefully sized for the specific reactions involved and, as far as possible, was designed for optimum performance.

Although USI's allethrin production began in July 1952, operation at a capacity rate of about 6250 pounds per month was not attempted until May 1953. Because of the limitations of present demand, however, USI has not continued its production at this capacity level.

The complexity of the USI plant is suggested by the fact that the process involves the use of 130 reactors, receivers, and holding tanks, as well as 80 pumps, more than 100 recording and controlling instruments, and close to 10 miles of piping. For production at design capacity, the plant requires nearly 1,000,000 pounds of chemicals per month. As standard procedure, the plant laboratory must analyze more than 35 different raw materials and some 20 intermediates, by-products, and solvents.

Allethrin production at USI takes place in two buildings. The main building, which is a two-story unit containing about 85% of the plant equipment, covers an area of 67 × 165 feet. The smaller building, which is reserved for hazardous reactions, is an L-shaped structure, two of whose major dimensions are 25 and 55 feet.

Batch Procedures Are Used in Most of the Process Steps at USI's Baltimore Plant

USI's allethrin operation is a batch process for virtually all products isolated. The single exception is the synthesis of 2,5-dimethyl-2,4-hexadiene. Since a principal objective has been to keep all of the equipment in operation as much of the time as possible, the batch size in each process step is not necessarily equivalent to one run of allethrin. For example, where a particular step involves an unusually long time cycle, it may be carried out on material equivalent to several runs of allethrin. The details of the process are indicated in Tables II and III.

In its synthesis of allethrin, USI uses the 18 steps outlined in Figure 1.

First Series of Chemical Reactions Involves Synthesis of Allethrolone

The allethrin process, outlined in Figures 2 and 3, begins with the synthesis of ethyl α-allyl acetoacetate, an intermediate in the production of allyl acetone. This initial step consists of the reaction of sodium ethyl acetoacetate with an excess of allyl chloride. The crude sodium ethyl acetoacetate, produced at USI's Baltimore plant, consists of a slurry containing about 19% sodium ethyl acetoacetate, 10% ethyl alcohol, and the remainder ethyl acetate.

In the initial step, allyl chloride and crude ethyl acetoacetate are added to reactor 1. The progress of the reaction is followed by a periodic analysis of samples. Near the end of the reaction, the mixture is heated at atmospheric pressure to reflux temperature to force the reaction as near to completion as possible.

When the reaction is complete, the ethyl acetate is stripped off at atmospheric pressure, initially without reflux, although moderate reflux is used toward the end of the distillation. The distilled ethyl acetate passes through a short, packed column and

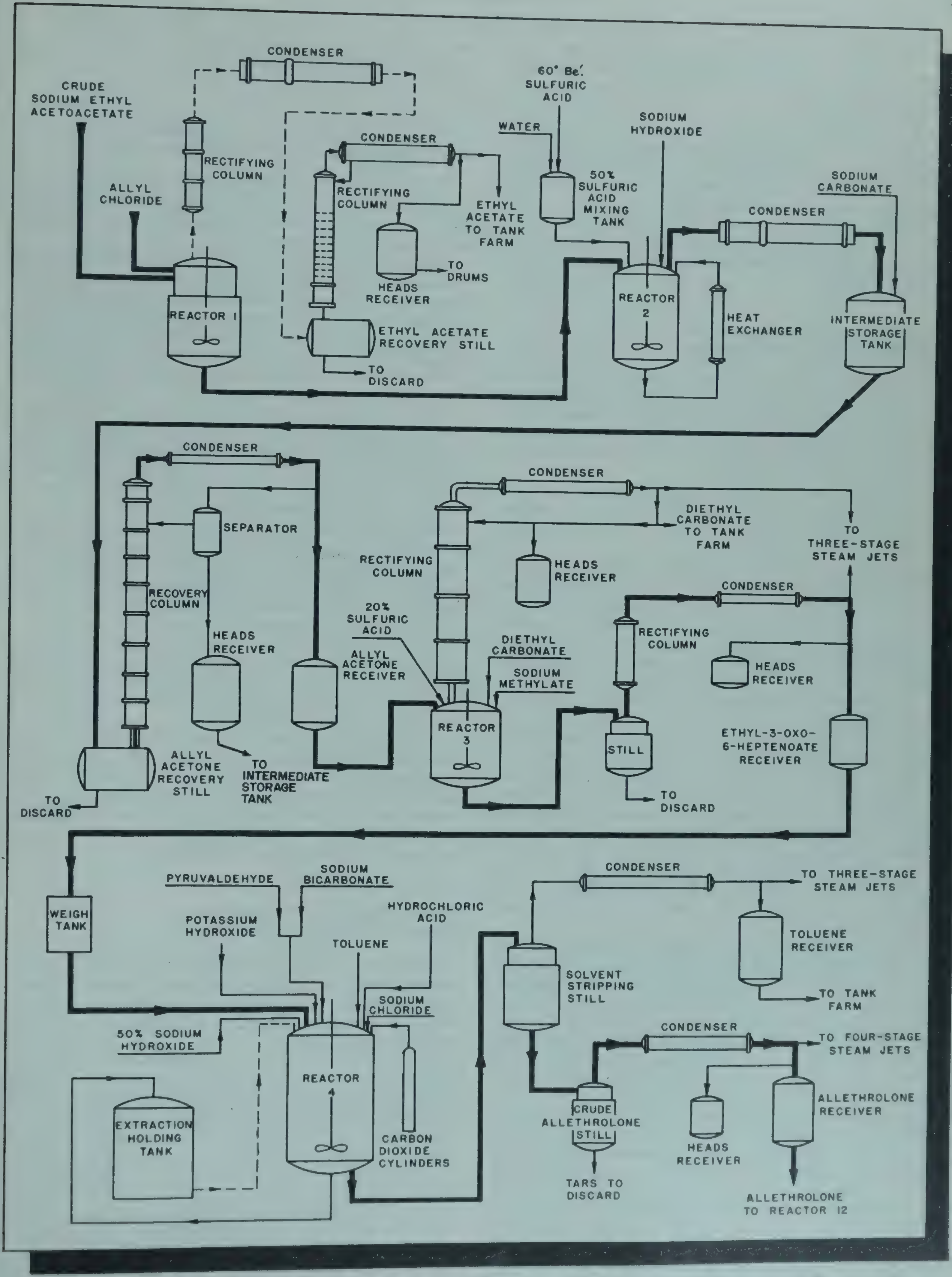

CRUDE SODIUM ETHYL ACETOACETATE
ALLYL CHLORIDE
CONDENSER
RECTIFYING COLUMN
REACTOR 1
CONDENSER
RECTIFYING COLUMN
ETHYL ACETATE TO TANK FARM
HEADS RECEIVER
TO DRUMS
ETHYL ACETATE RECOVERY STILL
TO DISCARD
60° Bé. SULFURIC ACID
WATER
SODIUM HYDROXIDE
50% SULFURIC ACID MIXING TANK
REACTOR 2
HEAT EXCHANGER
CONDENSER
SODIUM CARBONATE
INTERMEDIATE STORAGE TANK
CONDENSER
SEPARATOR
RECOVERY COLUMN
HEADS RECEIVER
ALLYL ACETONE RECOVERY STILL
TO DISCARD
TO INTERMEDIATE STORAGE TANK
ALLYL ACETONE RECEIVER
20% SULFURIC ACID
RECTIFYING COLUMN
CONDENSER
DIETHYL CARBONATE TO TANK FARM
TO THREE-STAGE STEAM JETS
HEADS RECEIVER
DIETHYL CARBONATE
SODIUM METHYLATE
REACTOR 3
CONDENSER
RECTIFYING COLUMN
HEADS RECEIVER
STILL
TO DISCARD
ETHYL-3-OXO-6-HEPTENOATE RECEIVER
WEIGH TANK
PYRUVALDEHYDE
SODIUM BICARBONATE
POTASSIUM HYDROXIDE
HYDROCHLORIC ACID
TOLUENE
SODIUM CHLORIDE
50% SODIUM HYDROXIDE
REACTOR 4
CARBON DIOXIDE CYLINDERS
EXTRACTION HOLDING TANK
CONDENSER
TO THREE-STAGE STEAM JETS
SOLVENT STRIPPING STILL
TOLUENE RECEIVER
TO TANK FARM
CONDENSER
TO FOUR-STAGE STEAM JETS
CRUDE ALLETHROLONE STILL
TARS TO DISCARD
HEADS RECEIVER
ALLETHROLONE RECEIVER
ALLETHROLONE TO REACTOR 12

Figure 2. Flow Sheet for the Production of Allethrolone at Baltimore, Md., Plant of U. S. Industrial Chemicals Co.

then to the ethyl acetate recovery still. The initial fraction from this still contains mainly allyl chloride and ethyl acetate, while the subsequent fraction consists of ethyl acetate free of chloride and containing about 10% ethyl alcohol. The tarry residue in the still is discarded.

After the material in reactor 1 is stripped of ethyl acetate, it goes to reactor 2 for treatment with 5% sodium hydroxide to produce sodium α-allyl acetoacetate and ethyl alcohol. First, however, a laboratory saponification test is carried out to determine the exact amount of caustic required.

After saponification, the material in reactor 2 is acidified with 50% sulfuric acid to convert the sodium α-allyl acetoacetate to allyl acetone, with the simultaneous formation of sodium bisulfate and carbon dioxide.

Atmospheric Distillation Employed in Purification of Crude Allyl Acetone

The allyl acetone is then purified. Reactor 2 is heated long enough to distill over all the allyl acetone into the intermediate storage tank. The distillate comes over as a constant-boiling mixture with water at 91° C. At the end of the distillation, the residue, containing water, sodium bisulfate, and other inorganic salts, is neutralized and discarded.

The material collected in the intermediate storage tank consists mainly of allyl acetone, water, and ethyl alcohol in addition to some acetic acid formed by side reactions. Sodium carbonate is added to neutralize the acid.

The allyl acetone recovery still is charged with all the crude allyl acetone from the preceding step. The initial distillate, consisting mainly of wet ethyl alcohol and allyl acetone, is collected in a separate receiver and returned to the intermediate storage tank.

The main fraction, consisting of wet allyl acetone, is subsequently redistilled. After the water is removed, the overhead temperature rises to 127° C., and allyl acetone of 99.5% purity is collected as product. The small quantity of still residue is discarded.

Next, the allyl acetone goes to reactor 3, where it is treated with diethyl carbonate to form ethyl-3-oxo-6-heptenoate and ethyl alcohol. The diethyl carbonate, produced at the Baltimore plant, must contain no more than 0.1% water since the sodium methylate employed in this reaction is decomposed by water.

After the diethyl carbonate and sodium methylate are added, the reactor is heated to 60° C. and a 90-mm. vacuum is applied. The allyl acetone is then gradually drawn into the reactor by vacuum. The rate of addition of allyl acetone, observed on a rotameter, is governed by the rate of removal of alcohol formed by the reaction.

During this step, the alcohol is distilled into a heads receiver and later purified for re-use by the Baltimore plant. Once the reaction is complete, the batch is cooled to room temperature and acidified by the addition of 20% sulfuric acid. The acid breaks up the sodium complex of the heptenoate and produces the free ethyl-3-oxo-6-heptenoate. The aqueous phase is discarded, and the organic phase is washed twice with water to remove sodium sulfate and excess acid. Both washes are discarded.

A vacuum of 25 mm., produced by three-stage steam jets, is applied to the reactor, and the excess diethyl carbonate is distilled off. The wet diethyl carbonate, which comes over first, is collected in a heads receiver and returned to the plant for recovery. The distillate of dry diethyl carbonate that comes over next is collected in a separate receiver and is re-used in the next batch.

The crude ethyl-3-oxo-6-heptenoate is then fractionated in a separate still under a 14-mm. vacuum produced by three-stage steam jets. The initial fraction consists of a small amount of diethyl carbonate, in addition to some ethyl α-allyl acetoacetate formed in a side reaction during the synthesis of ethyl-3-oxo-6-heptenoate. The ethyl α-allyl acetoacetate collected in the heads receiver is subsequently returned to the process for conversion to allyl acetone. Ethyl-3-oxo-6-heptenoate is collected as product, and the tarry residue is discarded.

Ethyl-3-oxo-6-heptenoate Is Saponified at Room Temperature with Potassium Hydroxide

The product is then sent to a weigh tank, from which it is transferred to reactor 4. There, it is saponified with an excess of 10% potassium hydroxide to produce potassium-3-oxo-6-heptenoate and ethyl alcohol.

Carbon dioxide in the presence of water is used to convert the potassium-3-oxo-6-heptenoate to 3-oxo-6-heptenoic acid and potassium bicarbonate. Carbon dioxide rather than a conventional mineral acid is employed in this step since the potassium bicarbonate formed by the reaction serves as a convenient buffering agent. Since even a large excess of carbon dioxide will not produce a pH of less than 8, the possibility of product decomposition at low pH is prevented.

In the next step 37 to 43% pyruvaldehyde, obtained from an outside supplier, is treated with sodium bicarbonate to raise its pH from 3 to 8. This pyruvaldehyde is then added to the 3-oxo-6-heptenoic acid in reactor 4. The addition of pyruvaldehyde results in the formation of 3-hydroxy-8-nonene-2,5-dione, with the simultaneous evolution of carbon dioxide.

After the reaction is complete, the mixture is acidified with 35% hydrochloric acid, which drives off the dissolved carbon dioxide. Next, 50% sodium hydroxide is added to raise the pH to a minimum of 10.0. The caustic converts the dione to 2-allyl-3-methyl-2-cyclopenten-4-olone, or allethrolone. This product is one of the two major intermediates in the allethrin process.

In the synthesis of allethrolone, an aliphatic compound is transformed into a cyclic compound, with the formation of water. At the completion of the reaction, the solution is acidified with hydrochloric acid, and the allethrolone is salted out of solution by the addition of sodium chloride.

Next, the aqueous phase is extracted with toluene. The two phases are stirred for 15 to 20 minutes and then allowed to settle for 30 minutes. The aqueous phase is transferred to a holding tank, and the organic phase is sent to the solvent stripping still. The extraction of the aqueous phase is carried out three additional times with toluene. The toluene extracts are sent to the stripping still, and the final water layer is discarded.

Vacuum Operation Minimizes the Thermal Breakdown of Allethrolone

The solvent stripping still is heated to about 55° C. to distill off the toluene. Vacuum operation, employing three-stage steam jets, is used to minimize thermal decomposition of the allethrolone. The toluene is collected in a refrigerated receiver and then sent to the tank farm.

Next, the crude allethrolone is transferred to the allethrolone still, operated at 0.4- to 0.7-mm. vacuum produced by four-stage steam jets. After the low boiling material has distilled over, the product is collected in a separate receiver within a 6° C. temperature range, the exact temperatures being a function of the operating pressure. For example, if the pressure is 0.5 mm., the allethrolone is collected between 101° and 107° C. The product is subsequently stored in 55-gallon stainless steel drums, and each drum is analyzed separately for allethrolone content.

The product contains 90 to 95% allethrolone, with the remainder consisting of a mixture of by-products. Allethrolone of this purity produces allethrin of approximately the same purity. The USI plant is equipped to produce allethrolone of whatever purity is needed for the production of whatever grade of allethrin is specified by the customer.

Table II. Major Reactions

Reaction No.	Preparation of	Reactants	Source of Reactant	Process Equipment Used	Reaction Temp., ° C.	Reaction Pressure	Remarks
1	Ethyl α-allyl acetoacetate	19% Sodium ethyl acetoacetate Allyl chloride	Steel measuring tank Steel scale tank	Reactor 1, steel, agitated, jacketed	Room	Atm.	Sodium chloride by-product
2	Sodium α-allyl acetoacetate	Ethyl α-allyl acetoacetate 5% Sodium hydroxide	Reactor 1 Steel storage tank	Reactor 2, nonferrous, agitated, outside heat exchanger	Room	Atm.	Ethyl alcohol by-product
3	Allyl acetone	Sodium α-allyl acetoacetate 50% Sulfuric acid (to pH 3)	Reactor 2 Lead - lined mixing tank	Reactor 2	Room	Atm.	Sodium bisulfate and carbon dioxide by-products
4	Ethyl-3-oxo-6-heptenoate	Allyl acetone Diethyl carbonate In presence of sodium methylate	Drum Tank farm Drum	Reactor 3, nonferrous, agitated, internal coils for steam or water	60	90 mm.	Reaction must be anhydrous; end indicated when vapor temp. rises; ethyl alcohol by-product
5	Potassium-3-oxo-6-heptenoate	Ethyl-3-oxo-6-heptenoate 10% Potassium hydroxide	Aluminum weigh tank Steel storage tank	Reactor 4, steel, agitated, internal coils, outside heat exchanger	Room	Atm.	Potassium hydroxide used is slightly more than that required for saponification; ethyl alcohol by-product
6	3-Oxo-6-heptenoic acid	Potassium-3-oxo-6-heptenoate Carbon dioxide Water	Reactor 4 Cylinders Already present	Reactor 4	Room	Atm.	Carbon dioxide added to liberate product; reaction to pH 8; $KHCO_3$ by-product
7	3-Hydroxy-8-nonene-2,5-dione	3-Oxo-6-heptenoic acid About 37% pyruvaldehyde	Reactor 4 Aluminum weigh tank	Reactor 4	Room	Atm.	Reaction at pH 8; pyruvaldehyde adjusted to pH 8 before addition; CO_2 by-product
8	Allethrolone	3-Hydroxy-8-nonene-2,5-dione In presence of 50% sodium hydroxide	Reactor 4 Steel storage tank	Reactor 4	20	Atm.	Alkaline cyclization; H_2O by-product
9	2,5-Dimethylhexyne-2,5-diol	Acetylene Acetone Potassium hydroxide Hydrochloric acid In presence of toluene and catalyst	Cylinders Steel storage tank Drums Rubber-lined tank	Reactor 5, steel, agitated, jacketed; and stripping still, glass-lined, agitated, jacketed	20	Atm.	Acid added at end of reaction; KCl by-product
10	2,5-Dimethylhexane-2,5-diol	2,5-Dimethylhexyne-2,5-diol Hydrogen Ni catalyst in presence of toluene	Fiber drums Cylinders	Reactor 6, steel, agitated, jacketed	90	100 lb./sq. inch	At start, temperature of exothermic reaction controlled with cooling water
11	2,5-Dimethyl-2,4-hexadiene	2,5-Dimethylhexane-2,5-diol	Fiber drums	Catalyst tube, heated with Dowtherm	...	Atm.	Catalytic dehydration is carried out continuously
12	Ethyl glycine hydrochloride	Glycine Ethyl alcohol Hydrogen chloride	Fiber drums Steel storage tank Cylinders	Reactor 7, glass-lined, agitated, jacketed	60	Atm.	Anhydrous alcohol used; H_2O by-product
13	Ethyl diazoacetate	Ethyl glycine hydrochloride Sodium nitrite 60° Bé. sulfuric acid Water	Fiber drums Drums Drums Line	Reactor 8, glass-lined, agitated, jacketed	20–24	Atm.	Careful temperature control; reaction conducted behind barricade; HCl and H_2O by-products

Preparation of Chrysanthemum Acid Chloride Is Second Major Phase of Allethrin Synthesis

The second phase of the allethrin process involves the preparation of chrysanthemum acid chloride, which is reacted with allethrolone to form allethrin. The preparation of chrysanthemum acid chloride requires the prior synthesis of 2,5-dimethyl-2,4-hexadiene and ethyl diazoacetate.

The initial step in the production of 2,5-dimethyl-2,4-hexadiene involves the formation of 2,5-dimethylhexyne-2,5-diol. In the synthesis of 2,5-dimethylhexyne-2,5-diol, acetylene reacts with potassium hydroxide to form potassium acetylide, which, in turn, combines with acetone to form the potassium salt of 2,5-dimethylhexyne-2,5-diol. The free 2,5-dimethylhexyne-2,5-diol is then obtained by treatment of the potassium salt with hydrochloric acid.

To reactor 5, toluene, solid potassium hydroxide, and a catalyst are added. Next, acetylene and acetone are charged simultaneously. Since any surplus of acetone will react with the potassium hydroxide to form an unwanted aldol-type polymer, care is taken to maintain a small excess of acetylene in the reactor at all times.

After all the reactants have been charged, agitation is continued for one hour at 20° C., and water is added. The water, which forms an emulsion, picks up most of the potassium hydroxide. Next, hydrochloric acid is added to lower the pH from 11 to 7. The potassium chloride produced by the reaction appears in crystalline form dispersed throughout the batch.

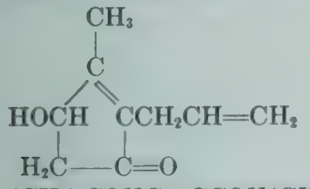
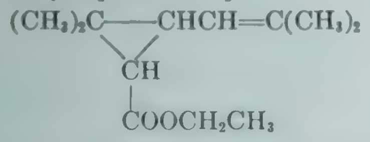
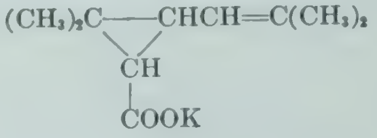
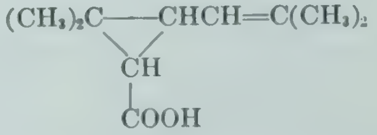
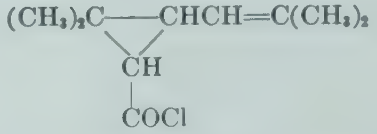
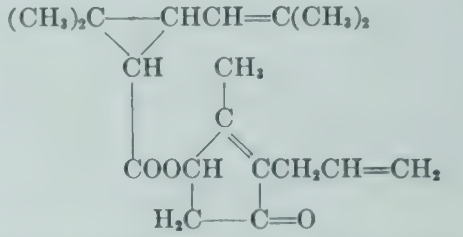
The contents of the reactor are then transferred to a glass-lined stripping still, where hydrochloric acid is added to reduce the pH from 7 to 5. The final adjustment of the pH to 5 is made in the glass-lined still rather than in the steel reactor to avoid corrosion.

The contents of the still are then heated to 75° C. with agitation to dissolve the 2,5-dimethylhexyne-2,5-diol in the toluene phase, while the potassium chloride goes into solution in the aqueous phase. Once the temperature has reached 75° C., the agitation is stopped, the batch is allowed to settle for 30 minutes, and the aqueous phase is discarded to the sewer. The organic phase is then distilled to remove most of the toluene. The still residue contains the 2,5-dimethylhexyne-2,5-diol dissolved in toluene. The still is then cooled from 115° to 85° C., and the contents are sent to a crystallizer equipped with a brine jacket operated at 10° C.

After the 2,5-dimethylhexyne-2,5-diol is cooled to 10° to 15° C., it flows by gravity through a neoprene hose to a Büchner-type filter, where it is freed of most of the entrained liquid. The filter cake is then washed with toluene and dried in place by

Table II. Major Reactions (*Continued*)

Reaction No.	Preparation of	Reactants	Source of Reactant	Process Equipment Used	Reaction Temp., ° C.	Reaction Pressure	Remarks
14	Ethyl chrysanthemumate	Ethyl diazoacetate 2,5-Dimethyl-2,4-hexadiene Copper catalyst	Stripping still Drums	Reactor 9, alloy steel, agitated, jacketed	130–140	Atm.	Reaction conducted behind barricade; nitrogen by-product
15	Potassium chrysanthemumate	Ethyl chrysanthemumate Potassium hydroxide In presence of ethyl alcohol	Receiver or drums	Reactor 10, alloy, agitated, jacketed	78	Atm.	Ethyl alcohol added to aid saponification; ethyl alcohol by-product
16	Chrysanthemum acid	Potassium chrysanthemumate 50% Sulfuric acid In presence of heptane	Reactor 10 Storage tank	Reactor 10	20	Atm.	Sulfuric acid liberates the chrysanthemum acid; potassium sulfate by-product
17	Chrysanthemum acid chloride	Chrysanthemum acid Thionyl chloride	Reactor 10 Carboys	Reactor 11, glass-lined, agitated, jacketed	20	Atm.	Reaction must be anhydrous; HCl and SO_2 by-products
18	Allethrin	Chrysanthemum acid chloride Allethrolone In presence of benzene and pyridine	Carboys Drums	Reactor 12, glass-lined, agitated, jacketed	30	Atm.	Pyridine added to remove hydrogen chloride as formed

Reaction No.	Principal Reaction Product
1	$CH_3COCH(CH_2CH{=}CH_2)COOCH_2CH_3$
2	$CH_3COCH(CH_2CH{=}CH_2)COONa$
3	$CH_2{=}CHCH_2CH_2COCH_3$
4	$CH_2{=}CHCH_2CH_2COCH_2COOC_2H_5$
5	$CH_2{=}CHCH_2CH_2COCH_2COOK$
6	$CH_2{=}CHCH_2CH_2COCH_2COOH$
7	$CH_2{=}CHCH_2CH_2COCH_2CHOHCOCH_3$
8	
9	$(CH_3)_2COHC{\equiv}CCOH(CH_3)_2$
10	$(CH_3)_2COHCH_2CH_2COH(CH_3)_2$
11	$(CH_3)_2C{=}CHCH{=}C(CH_3)_2$
12	$CH_3CH_2OOCCH_2NH_2HCl$
13	$CH_3CH_2OOCCHN_2$
14	
15	
16	
17	
18	

blowing with hot air. The dry 2,5-dimethylhexyne-2,5-diol, a white crystalline solid with a melting point of 93° to 95° C., is stored temporarily in fiber drums.

The filtrate and washings from three filtrations are later combined and concentrated by removal of toluene. The 2,5-dimethylhexyne-2,5-diol is crystallized to form a white or light-tan solid having slightly lower purity than that of the initial product. Ordinarily, this secondary product is of sufficient purity to be used directly. If not, it is redissolved in toluene, treated with activated charcoal, filtered, recrystallized, refiltered, washed, dried, and returned to the process.

Nickel Catalyst Aids Hydrogenation of the 2,5-Dimethylhexyne-2,5-diol

The next step involves the catalytic hydrogenation of 2,5-dimethylhexyne-2,5-diol to 2,5-dimethylhexane-2,5-diol. First 2,5-dimethylhexyne-2,5-diol and toluene are added to reactor 6. Toluene rather than alcohol or benzene is preferred as a solvent because of its higher flash point and lower toxicity. In subsequent recovery operations, essentially equal yields are obtained.

The reactor is heated to about 70° C., and a nickel catalyst is added. Before hydrogen is admitted to the system, the reactor is purged with nitrogen to remove oxygen that might form an explosive mixture with hydrogen. In the purging operation, the nitrogen pressure is first raised to 50 pounds per square inch. The gas is then vented to the atmosphere, and the procedure repeated twice. The same operation is then carried out twice with hydrogen. After the second hydrogen purge, the hydrogen pressure is increased to 100 pounds per square inch. Ordinarily in purging, the procedure is to apply vacuum to the system and then add the nitrogen. However, vacuum cannot be used in this step since the 2,5-dimethylhexyne-2,5-diol would sublime and plug the vacuum jets.

The progress of the reaction is followed by the periodic removal of samples, which are tested for unsaturation by treatment with bromine water. Before the hydrogenation is stopped, however, a sample is taken, filtered, dried, and tested for melting point.

The contents of the hydrogenator, at about 90° C., are then sent to a brine-jacketed crystallizer. Along the way, the solution passes through a filter to remove the nickel catalyst, which is discarded.

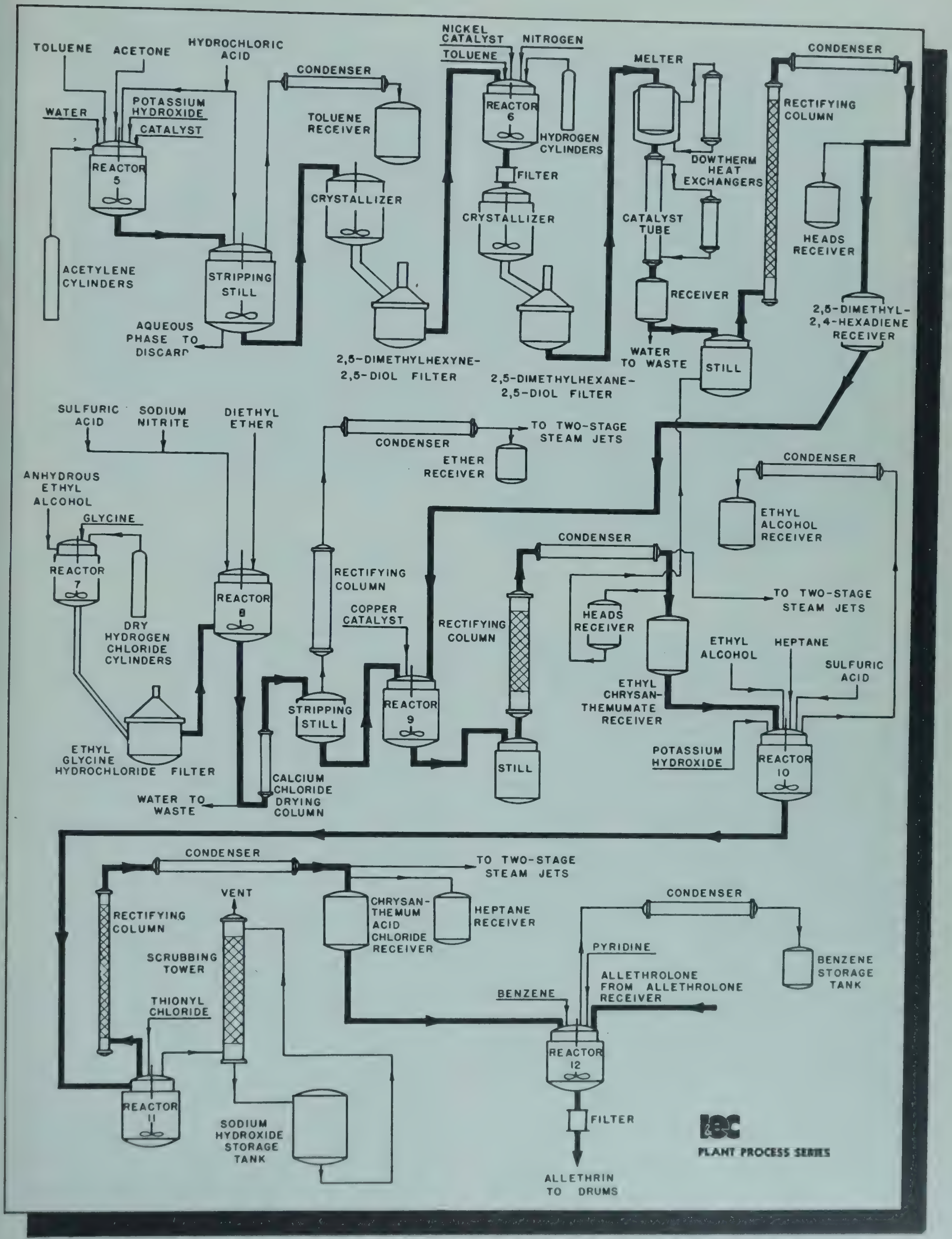

TOLUENE
ACETONE
HYDROCHLORIC ACID
WATER
POTASSIUM HYDROXIDE
CATALYST
REACTOR 5
ACETYLENE CYLINDERS
CONDENSER
TOLUENE RECEIVER
CRYSTALLIZER
STRIPPING STILL
AQUEOUS PHASE TO DISCARD
2,5-DIMETHYLHEXYNE-2,5-DIOL FILTER
NICKEL CATALYST
NITROGEN
TOLUENE
REACTOR 6
HYDROGEN CYLINDERS
FILTER
CRYSTALLIZER
2,5-DIMETHYLHEXANE-2,5-DIOL FILTER
MELTER
DOWTHERM HEAT EXCHANGERS
CATALYST TUBE
RECEIVER
WATER TO WASTE
STILL
CONDENSER
RECTIFYING COLUMN
HEADS RECEIVER
2,5-DIMETHYL-2,4-HEXADIENE RECEIVER
SULFURIC ACID
SODIUM NITRITE
DIETHYL ETHER
ANHYDROUS ETHYL ALCOHOL
GLYCINE
REACTOR 7
DRY HYDROGEN CHLORIDE CYLINDERS
ETHYL GLYCINE HYDROCHLORIDE FILTER
REACTOR 8
WATER TO WASTE
CALCIUM CHLORIDE DRYING COLUMN
CONDENSER
TO TWO-STAGE STEAM JETS
ETHER RECEIVER
RECTIFYING COLUMN
COPPER CATALYST
STRIPPING STILL
REACTOR 9
RECTIFYING COLUMN
STILL
CONDENSER
HEADS RECEIVER
ETHYL CHRYSANTHEMUMATE RECEIVER
TO TWO-STAGE STEAM JETS
CONDENSER
ETHYL ALCOHOL RECEIVER
ETHYL ALCOHOL
HEPTANE
SULFURIC ACID
POTASSIUM HYDROXIDE
REACTOR 10
CONDENSER
TO TWO-STAGE STEAM JETS
RECTIFYING COLUMN
VENT
SCRUBBING TOWER
THIONYL CHLORIDE
REACTOR 11
SODIUM HYDROXIDE STORAGE TANK
CHRYSANTHEMUM ACID CHLORIDE RECEIVER
HEPTANE RECEIVER
CONDENSER
PYRIDINE
BENZENE STORAGE TANK
ALLETHROLONE FROM ALLETHROLONE RECEIVER
BENZENE
REACTOR 12
FILTER
ALLETHRIN TO DRUMS
I&EC
PLANT PROCESS SERIES

Figure 3. Flow Sheet for the Production of Allethrin at Baltimore, Md., Plant of U. S. Industrial Chemicals Co.

Table III. Distillations

Material Distilled	Distillation Equipment	Temp., ° C.	Pressure	Initial Fraction	Receiver for Initial Fraction	Second Fraction	Receiver for Second Fraction
Crude ethyl acetate	Copper kettle with bayonet heaters and column	To 78	Atm.	Mainly allyl chloride and ethyl acetate	Nonferrous	Ethyl acetate and ethyl alcohol	Nonferrous
Crude allyl acetone	Reactor 2, nonferrous, jacketed	To 100	Atm.	Allyl acetone, water, ethyl alcohol, and acetic acid	Steel	.....	.....
Distilled allyl acetone	Copper kettle, jacketed, and column	To 127	Atm.	Wet ethyl alcohol and allyl acetone	Nonferrous	99.5% Allyl acetone	Nonferrous
Ethyl alcohol in crude ethyl-3-oxo-6-heptenoate	Reactor 3, nonferrous, jacketed, and column	To 65	90 mm.	Methyl and ethyl alcohols	Steel	.....	.....
Diethyl carbonate in crude ethyl-3-oxo-6-heptenoate	Reactor 3	To 90	25 mm.	Wet mixed carbonates	Steel	Diethyl carbonate	Tank farm
Crude ethyl-3-oxo-6-heptenoate	Alloy steel kettle, jacketed, and column	To 110	14 mm	Diethyl carbonate and ethyl α-allyl acetoacetate	Alloy steel	Ethyl-3-oxo-6-heptenoate and ethyl α-allyl acetoacetate	Alloy steel
Toluene in crude allethrolone	Steel kettle, jacketed	To 55	75 mm.	Toluene	Steel	.....	.....
Distilled allethrolone	Alloy steel kettle, jacketed	101–107 for product cut	0.5 mm.	Low boiling materials	Alloy steel	Allethrolone	Alloy steel
Toluene in crude 2,5-dimethylhexyne-2,5-diol	Glass-lined kettle, jacketed, and column	To 115	Atm.	Toluene	Steel	.....	.....
Crude 2,5-dimethyl-2,4-hexadiene	Steel kettle, jacketed, and column	134–135 for product cut	Atm.	Mainly decomposition products of 2,5-dimethylhexane-2,5-diol	Steel	2,5-Dimethyl-2,4-hexadiene	Steel
Diethyl ether in crude ethyl diazoacetate	Glass-lined kettle, jacketed	To 15	100 mm.	Diethyl ether	Steel	.....	.....
Crude ethyl chrysanthemumate	Alloy steel kettle, jacketed, and column	To 70 initially, then to 95	60 mm. initially, then 10 mm.	2,5-Dimethyl-2,4-hexadiene	Steel	Ethyl chrysanthemumate	Alloy steel
Ethyl alcohol in crude potassium chrysanthemumate	Reactor 10, alloy, jacketed	To 100	Atm.	Ethyl alcohol and water	Steel	.....	.....
Crude chrysanthemum acid chloride	Reactor 11, glass-lined, jacketed, and column	93–100 for product cut	90 mm initially then 10 mm.	Heptane	Glass-lined	Chrysanthemum acid chloride	Glass-lined
Benzene in crude allethrin	Reactor 12, glass-lined, jacketed	To 50	10 mm.	Benzene	Steel	.....	.....

After cooling to 10° to 15° C. in the crystallizer, the 2,5-dimethylhexane-2,5-diol is filtered, washed with toluene, dried in place with hot air, and stored temporarily in fiber drums. The melting point of this material is 88° to 90° C. As in the case of the 2,5-dimethylhexyne-2,5-diol, the filtrate and washings are processed for the recovery of a second crop of crystals.

The synthesis of 2,5-dimethyl-2,4-hexadiene involves the catalytic dehydration of 2,5-dimethylhexane-2,5-diol. The 2,5-dimethylhexane-2,5-diol, heated to 100° to 115° C. in a melter, flows by gravity through a Dowtherm-heated catalyst tube. The temperature of this tube is checked periodically by thermocouples at three points. The reaction products flow into a receiver, from which the water layer is separated and discarded.

The organic phase is then distilled. The initial distillate contains the decomposition products of 2,5-dimethylhexane-2,5-diol in addition to a small amount of water. The product cut, collected in a separate receiver, contains the 2,5-dimethyl-2,4-hexadiene.

Ethyl Glycine Hydrochloride Is An Intermediate in the Preparation of the Ethyl Diazoacetate

The next series of steps involves the preparation of ethyl diazoacetate through the intermediate formation of ethyl glycine hydrochloride. In the synthesis of ethyl glycine hydrochloride, use is made of glycine, ethyl alcohol, and hydrogen chloride.

First, glycine and anhydrous alcohol are added to reactor 7. Dry hydrogen chloride gas is then bubbled through the mixture, and the reactants are heated under reflux until the reaction is complete. The material is then cooled to 20° to 25° C. with cooling water and dropped to a Büchner-type filter. The ethyl glycine hydrochloride is washed twice with anhydrous ethyl alcohol, dried in place with hot air, and stored temporarily in fiber drums. The product has a melting point of 142° to 144° C. The filtrate and washings, after neutralization with 5% sodium hydroxide, are discarded.

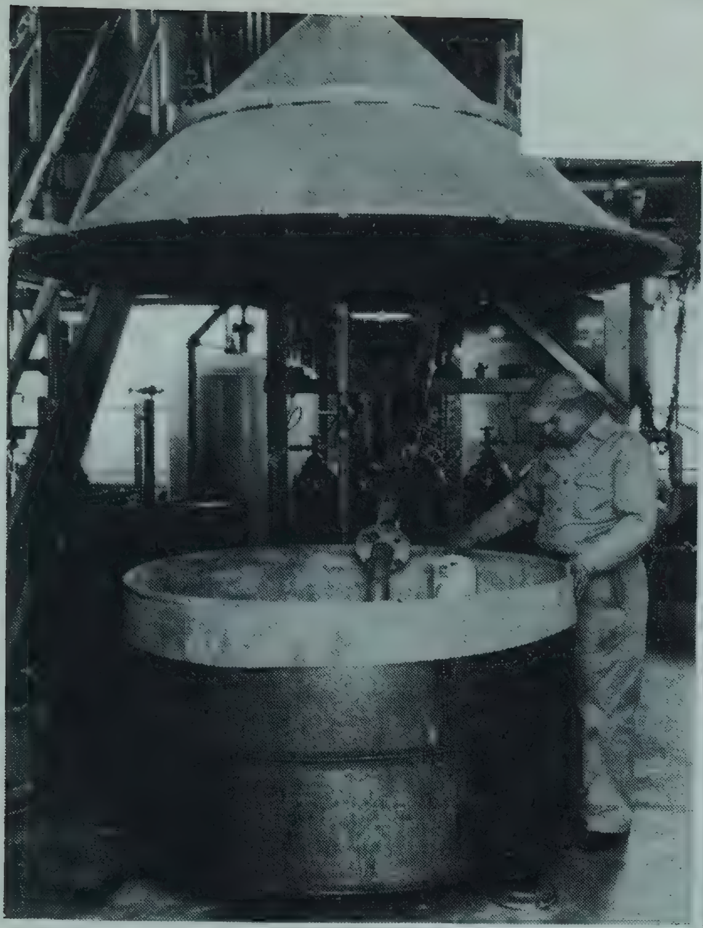
The ethyl glycine hydrochloride is then reacted with nitrous acid to form ethyl diazoacetate. After the ethyl glycine hydrochloride has been charged to reactor 8, water and diethyl ether are added to produce a slurry that can conveniently be mixed. Nitrous acid is produced by reacting aqueous sodium nitrite with sulfuric acid, both of which are metered individually by proportioning pumps into a single pipe leading to the reactor.

Reactor 8 is cooled with brine to maintain the diazotization temperature at 20° to 24° C. Careful temperature control is important in this step If the temperature rises above 24° C., there is danger that the ethyl diazoacetate formed by the reaction will begin to decompose rapidly with the evolution of large volumes of nitrogen. If the nitrogen cannot be vented quickly enough, there is the possibility of explosion. If the temperature rises excessively, the pumps controlling the flow of sulfuric acid and aqueous sodium nitrite are automatically shut off.

On the other hand, if the temperature drops below 18° C., there is danger that the reaction will stop altogether and an excess of nitrous acid will accumulate. The result may be a sudden resumption of the reaction with possibly explosive violence. If the reaction temperature falls to 18° C., the pump controlling the circulation of brine automatically stops.

To minimize the hazards of diazotization, numerous safety precautions are taken. The reaction is carried out in a special diazo building constructed of 14-inch reinforced concrete and isolated from the main allethrin building. While the reaction is in progress, the operators view the processing equipment from behind a special wall provided with one-inch-thick safety-glass windows. Once the diazotization has begun, no one is allowed inside the reaction room.

All valve handles extend through the barricade wall to permit

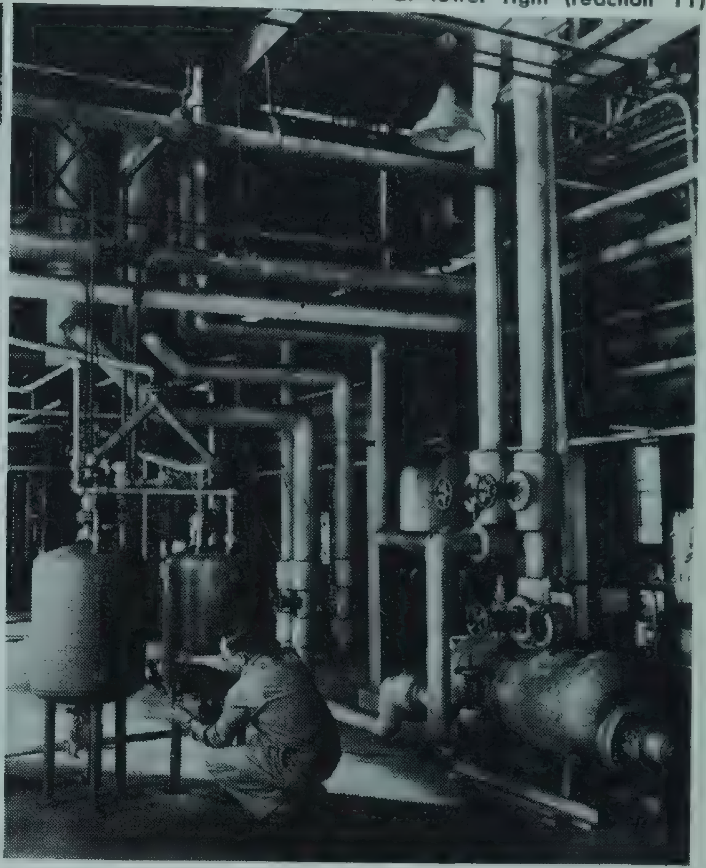


Büchner-Type Funnel Filters 2,5-Dimethylhexyne-2,5-diol

After filtration and washing, the cover is lowered and hot air is blown over the product until dry. This type of filter is also used for 2,5-dimethylhexane-2,5-diol and ethyl glycine hydrochloride

Two Receivers Are Used Alternately to Collect 2,5-Dimethyl-2,4-hexadiene and Water

Catalytic dehydration tubes are at upper left, and automatically controlled Dowtherm boiler at lower right (reaction 11)



the reaction to be controlled from outside the reaction room. In addition, all electrical equipment inside the reaction room is controlled by outside switches, each of which has its own pilot light to enable the operator to tell at a glance what equipment is in operation.

The roof of the diazo building is hinged so that it will readily swing upward in the event of an explosion. Moreover, the outside wall facing a free area is made of thin corrugated iron which, in case of an explosion, will quickly give way to produce a minimum of damage. Because of the fire hazard, the reaction room is equipped with 12 carbon dioxide fire extinguishers that can be turned on either automatically or manually from outside the room.

Aqueous Phase Extraction with Ether Recovers Ethyl Diazoacetate

Upon completion of the diazotization, the mixture is agitated for 30 minutes, and the organic phase, containing most of the ethyl diazoacetate, is sent to a vacuum stripping still. The aqueous phase is subsequently extracted three times with diethyl ether to remove the dissolved ethyl diazoacetate. The final water layer is discarded, and the combined ether extracts are sent to the stripping still. Before any of the organic material reaches the still, however, it passes through a calcium chloride drying column to eliminate the last traces of water.

Low-temperature distillation is used in the removal of diethyl ether to minimize the decomposition of the ethyl diazoacetate. Because of the instability of this compound, it goes immediately to the next step in the process—namely, the reaction of ethyl diazoacetate with 2,5-dimethyl-2,4-hexadiene to form ethyl chrysanthemumate with the evolution of nitrogen. Because of the explosion hazards involved in this coupling step, it also is carried out behind the barricade in the diazo room.

To reactor 9 are added 2,5-dimethyl-2,4-hexadiene and a finely divided copper catalyst. The mixture is then heated to reflux at atmospheric pressure. From a separate holding tank, all the ethyl diazoacetate produced in the previous step is gradually added to this mixture.

Upon completion of the reaction, the material is cooled to 20° C and pumped to a still operated initially at 60-mm. pressure, provided by two-stage steam jets. The excess hexadiene is then distilled off at 60-mm. pressure up to 90° C. The distillate is collected in a heads receiver and from there goes to the atmospheric still used in the earlier purification of the hexadiene.

Distillation of Ethyl Chrysanthemumate Is Carried Out at 10-Mm. Pressure

At 10-mm. pressure, the ethyl chrysanthemumate is distilled into the product receiver. The distillate then goes to reactor 10, where it is saponified with potassium hydroxide to form potassium chrysanthemumate and ethyl alcohol. Since this reaction and those that follow are essentially nonhazardous, they are carried out in the main allethrin building.

In addition to ethyl chrysanthemumate, reactor 10 is charged with ethyl alcohol, solid potassium hydroxide, and water. The reactants are refluxed until saponification is complete, and then the ethyl alcohol is distilled off at atmospheric pressure.

The contents of reactor 10 are subsequently cooled to 20° C., and the material is acidified by the addition of 50% sulfuric acid. The acid converts the potassium chrysanthemumate to chrysanthemum acid.

Next, heptane is added. The chrysanthemum acid goes into solution in the heptane layer, while the potassium sulfate remains dissolved in the water layer. The two phases are allowed to settle for 30 minutes, after which the water layer is drained to the sewer, and the organic layer goes to reactor 11.

The combined material in reactor 11 is then stripped of a small quantity of water by distillation at atmospheric pressure. After this drying step, the residue is processed without unnecessary delay. Otherwise, the cis form of chrysanthemum acid may precipitate out of solution and plug up the valves and pipelines.

First, however, a check is made on the absence of moisture in the reactor. All vents are equipped with silica gel drying tubes to prevent air from carrying moisture into the system. To the water-free material in reactor 11, containing about 30% chrysanthemum acid and 70% heptane, purified thionyl chloride is added to convert the chrysanthemum acid to chrysanthemum acid chloride with the evolution of sulfur dioxide and hydrogen chloride.

The evolved sulfur dioxide and hydrogen chloride pass through a Karbate scrubbing tower filled with Raschig rings. In this tower a solution containing about 20% sodium hydroxide is continuously circulated. Periodically, this solution is discarded and replaced by fresh material.

After the reaction is complete, the heptane is stripped off at 90-mm. pressure. The pressure is then lowered to 10 mm., and the chrysanthemum acid chloride is distilled over at 93° to 100° C. into the product receiver. The acid chloride is subsequently stored in glass carboys until ready to be reacted with allethrolone to form allethrin.

Reaction of Chrysanthemum Acid Chloride and Allethrolone Produces the Final Product

Before the final reaction begins, the chrysanthemum acid chloride is analyzed for purity. To reactor 12 are added allethrolone, pyridine, and benzene. Then, chrysanthemum acid chloride dissolved in benzene is gradually added. The reaction occurs almost instantaneously with the formation of allethrin and hydrogen chloride. At the same time, the hydrogen chloride combines with the pyridine to produce pyridine hydrochloride. If the hydrogen chloride is not removed almost as rapidly as formed, the reaction will not go to completion, and the yield of allethrin will be low. Although other anhydrous acceptors of hydrogen chloride have been tried, pyridine is the most effective.

After all the chrysanthemum acid chloride is charged, the reactor contents are washed with water to remove the solid pyridine hydrochloride. This material dissolves in the aqueous layer, while the allethrin remains in the benzene phase. The aqueous layer is then drawn off into a still, where its pH is adjusted to 10 by the addition of sodium hydroxide to convert the pyridine hydrochloride to pyridine. This latter material is then extracted with benzene, and the benzene layer is distilled to recover purified pyridine, which is returned to the process.

After the contents of reactor 12 have been water-washed, they are treated three times with sodium carbonate solution to remove free acid. The organic layer, containing the allethrin, is washed twice with water to remove salts and reduce the pH. The benzene is then distilled off under vacuum at a temperature below 50° C.

The allethrin is sent through a polishing filter for the removal of small amounts of solid impurities and is then stored in 55-gallon aluminum drums. The product from three to six runs is combined in a glass-lined mixing tank to produce a blend of about 1000 to 2000 pounds.

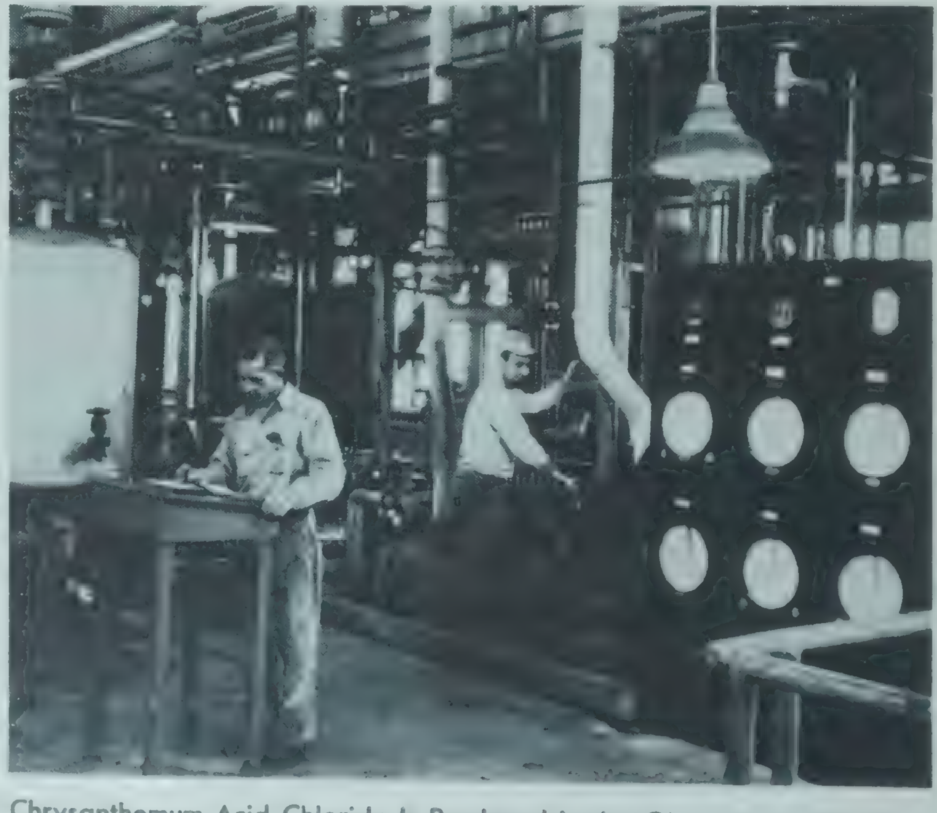
About 2 weeks is required for all 18 steps in the allethrin process to be completed. Each hour the plant uses approximately 500 pounds of steam, 60,000 gallons of cooling water, and 80 kilowatts of electrical power. The plant personnel needed for supervision, operation, and laboratory control totals 35 persons. The process is operated continuously around the clock, 7 days a week, each shift working an 8-hour day.

Either One of Two Standard Methods May Be Used in Analysis of Allethrin

The analytical laboratory runs tests on every batch of allethrin to determine the per cent by weight of allethrin, chrysanthemum acid, chrysanthemum acid chloride, chrysanthemum acid anhydride, color of allethrin, color of 10% solution, and appearance of 10% solution. For every blend consisting of several batches, not only are these tests run but also determinations of per cent by weight of Freon insolubles, specific gravity at 20°/20° C., and weight per gallon at 20° C. Biological activity tests are also run on each blend.

The content of pure allethrin in technical material can be determined by either of two generally accepted procedures—the hydrogenolysis method and the ethylenediamine method. The hydrogenolysis method depends on the cleavage of the ester by addition of hydrogen. The reaction takes place in isopropyl alcohol in the presence of a catalyst containing palladium oxide and barium sulfate. After the solution is filtered, the amount of chrysanthemum monocarboxylic acid formed by hydrogenolysis is measured by titration with alkali. Corrections are made for the free acidity originally present in the sample, as well as for the reagent blanks and for the catalyst activity.

In the more widely used ethylenediamine method (*14*), allethrin is reacted with ethylenediamine to form an equivalent amount of the amine salt of chrysanthemum monocarboxylic acid. The reaction ordinarily takes place at 25° to 30° C. for 2 hours. After pyridine is added, the chrysanthemum monocarboxylic acid formed is titrated with 0.1*N* sodium methylate in pyridine. Corrections are made for the reagent blanks and



Chrysanthemum Acid Chloride Is Produced in the Glass-Lined Still Near Control Panel

Alongside the still is ethyl chrysanthemumate distillation unit. Other equipment shown includes receivers and charging tanks for the chrysanthemum monocarboxylic acid, acid chloride, and acid anhydride initially present in the sample.

As yet, no general agreement has been reached on standard specifications for allethrin. The material intended for the armed forces, however, must contain at least 75% pure allethrin, and the free acid content must not exceed 8%. Although 2 and 3 years ago some of the allethrin produced commercially was only 75 to 80% pure, most of the allethrin available today is between 78 and 95% pure, while the free acid content is normally less than 1%.

Future Market for Allethrin Depends on Developmental Programs Now in Progress

As far as the future market for allethrin is concerned, the exact extent of this demand has been the subject of widely varying estimates. One prediction, for example, is somewhere in the neighborhood of 200,000 pounds a year. Much, of course, will depend on the future price of allethrin, as well as on government policies regarding chemical residues in foods. Much will also depend on the success of developmental programs now in progress.

As part of this developmental work, continued efforts are being made to devise new or expanded uses for allethrin. Allethrin is being tested for application to a wide range of farm crops, particularly near harvest. At the same time, the use of allethrin in insect-resistant packaging materials for cereals and other food products is being actively explored. One manufacturer is investigating the use of allethrin in livestock sprays containing the fly repellant, butoxypolypropylene glycol, which not only repells insects but also serves as an allethrin synergist.

As part of this ongoing research program, allethrin is being critically compared with other insecticides. In comparison to DDT, for example, allethrin shows superior knockdown against houseflies. In comparison to natural pyrethrum, allethrin gives virtually the same knockdown—approximately 94% in the standard Peet-Grady biological activity test (*4*). Allethrin is also the equal of pyrethrum in killing power. This essentially equal effectiveness of allethrin and pyrethrum against houseflies applies only, however, when each insecticide is used without a synergist. When allethrin is formulated with such a widely used synergist as piperonyl butoxide, it is only about one half as effective against flies as pyrethrum containing the same synergist. When used against roaches, allethrin plus synergist is only about one fourth as effective as pyrethrum plus synergist.

In some respects, however, allethrin is superior to pyrethrum. The synthetic insecticide has longer residual action and is more stable to ultraviolet light. Moreover, it can be manufactured in uniformly high purity and is free from the plant pigments, waxes, and other impurities present in natural pyrethrum extracts.

More specific in its action than pyrethrum, allethrin is effective against fewer different types of insects. This lesser effectiveness against such insects as roaches may be explained by the presence of several comparatively inert isomers in allethrin.

While attempting to overcome these handicaps, manufacturers are also making a concerted effort to develop new markets for allethrin intermediates (*13*). Increased application might be found for such compounds as allyl acetone, 2,5-dimethylhexane-2,5-diol, chrysanthemum monocarboxylic acid, and ethyl α-allyl acetoacetate. Today, sample quantities of these and other related intermediates are being widely distributed by allethrin manufacturers for test purposes (*9*).

As might be expected, much work is being directed toward the reduction of processing costs and the increase of product yields. Particular attention is being paid to the final step in the synthesis of allethrolone. Although this step is one of the most carefully controlled in USI's entire allethrin process, the percentage conversion is still relatively low.

In laboratory research, chemists are attempting to synthesize each of the eight stereoisomers of allethrin. Work is also being done on the synthesis and testing of compounds chemically related to allethrin. Among the most promising of these is furethrin, which contains a 2-furfuryl side chain (*15*) and whose toxicity to houseflies compares favorably with that of allethrin. The production of furethrin, which would involve the use of furfuryl acetone in place of the allyl acetone employed in the allethrin synthesis, is currently being investigated by USI.

Researchers Intensify Search for Improved Synergists to Expand Insecticide Markets

One of the most challenging aspects of allethrin research is the exploration of new compounds capable of increasing the insect-killing power of allethrin. The expanded use of allethrin against household crawling insects, for example, awaits only the discovery of practical new synergists capable of making allethrin at least the equal of synergized pyrethrum. Although several new, highly effective synergists have already been developed in the laboratory, their cost at present is prohibitive.

Though faced with a multitude of unsolved problems, manufacturers today express overwhelming confidence in the future of allethrin. In the words of one company spokesman: "Recent history has shown that any single insecticide—no matter how versatile or how highly touted—can never satisfy all our insecticidal needs. This is true of allethrin, as well as of all the others. However, allethrin does have a very real place in the nontoxic insecticide field. We look forward with assurance to an expanding program for its use."

Acknowledgment

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Spoked Wheel Breaks Sheet of Solidified Ammonium Nitrate as It Flows Off Cooling Belt

ALBERT S. HESTER, *Assistant Editor*

in collaboration with

J. J. DORSEY, Jr.
Commercial Solvents Corp., Sterlington, La.
J. T. KAUFMAN
Commercial Solvents Corp., Terre Haute, Ind.

Stengel Process Ammonium Nitrate

AMMONIUM nitrate's high nitrogen content, about 35% by weight, makes it one of the most concentrated nitrogen sources available for fertilizers. It is true that anhydrous ammonia has a higher proportion of nitrogen and in the last few years its direct application to the soil has increased but the rather extensive outlay of pressure vessels for storage and special equipment for application tends to restrict its use to the larger farms and those small farms where custom application is available at reasonable cost. Urea, which contains 46.6% nitrogen, is the only other chemical nitrogen source commercially available having a greater proportion of nitrogen, but it is more expensive on the basis of both weight and nitrogen content than ammonium nitrate. Ammonium sulfate and sodium nitrate, with approximately 20 and 16% nitrogen, respectively, round out the list of major nitrogen-bearing chemicals for fertilizers.

For the most part, ammonia manufacturers would be well satisfied if they could sell their fertilizer nitrogen in the form of anhydrous ammonia. No great profit is made in converting the ammonia to ammonium nitrate; the conversion is necessary merely to get the nitrogen into a solid form, which can be stored and applied using only those facilities found on an ordinary farm. From the manufacturer's point of view the solid salt may be stored much more easily than the liquid anhydrous ammonia. This is a very important consideration in such a seasonal business. Demand is heaviest from early spring until midsummer; then there is a sharp decline to a low level, broken only by a slight rise in the fall when pastures are treated.

Last year, an article in this series (*5*) described a prilling process for making ammonium nitrate. Prilling is one of the three more or less standard processes for preparing the salt. The other two methods are crystallization and graining. In all these processes ammonia and nitric acid react forming a solution of ammonium nitrate which is then concentrated by evaporation to obtain the solid salt. In the prilling process the hot concentrated solution is sprayed into the top of a tower through which a cooling current of air flows. The drops solidify into pellets or "prills" while falling through the tower.

Crystallization processes involve crystallizing from a saturated solution and separating crystals from the mother liquor by centrifuging. Graining is accomplished by evaporating the solution almost to dryness and then cooling at a controlled rate while the solidifying mass is stirred with heavy plows. Eventually the batch hardens into small rounded grains of ammonium nitrate.

In the manufacture of ammonium nitrate the low profit margin necessitates careful examination of costs from a standpoint of both initial investment and operating expenditures. The other prime consideration in a potential process is safety. The disasters at Texas City in 1947 and Oppau in Germany in 1923 were both results of ammonium nitrate explosions. In fact, before its use as a fertilizer was started in earnest in 1942, most of the ammonium nitrate output was for explosive purposes. However, by observing the same kind of precautions that are established for the safe handling of other oxidizing materials, large amounts are today safely transported and stored all over the continent with no disastrous results.

Stengel Process Has Many Advantages Over Older Processes

The reaction between ammonia and nitric acid is highly exothermic, but the danger inherent in handling large quantities of ammonium nitrate at temperatures near its melting point has heretofore always deterred those who sought to utilize this heat to drive off all the water from the solution in which the neutralization takes place. Only recently has this old problem been satisfactorily solved by Stengel (*6*), who employed a radically different approach. The process was tested in the laboratory and pilot plant, and now CSC has a full scale plant (225 tons per day) in production at Sterlington, La.

In this process ammonium nitrate containing any desired water content can be produced in a single step. The neutralization reaction takes place in a packed, tubular reactor. The molten ammonium nitrate collects on the packing, flows to the bottom of the reactor and through a centrifugal separator whose bottom portion is filled with packing. Air blown through the material flowing through the packing reduces the moisture content to almost any desired level. The liquid product is then ready for prilling, graining, or, in actual practice at CSC, flaking. The molten nitrate is covered with a blanket of steam from the time it forms until it leaves the separator. Because of this and the fact that the total hold up in the reactor at any one time is exceedingly small, the process is considered quite safe.

Compare the simplicity of this process with conventional procedures. In what is essentially one piece of equipment, the reactor, the raw materials react and molten ammonium nitrate, of very low moisture content, emerges. In other processes the neutralization reaction is carried out so that the ammonium nitrate is formed in a solution. The neutralizer for a plant of the same capacity must be much larger than the small reactor used in the Stengel process. More important, the solution must then be evaporated. Whether evaporation is to proceed to the salt concentrations of 98% for graining, 79% for crystallizing, or 81 to 95% for prilling (*5*), it is an expensive operation and requires a high equipment investment. In addition, the evaporation of large quantities of ammonium nitrate is always a potential hazard.

In the flaking process as carried out by Commercial Solvents molten ammonium nitrate flows onto one end of a continuous, stainless steel, water-cooled belt, and the solidified material is removed from the other end. It is then broken, ground, and screened. In this section of the process too, the amount of material held up in process at any time is small. It consists of only the contents of the weir box, the thin layer of nitrate on the cooling belts, the load on the conveying system, and the almost negligible quantity in the grinders and screen. While flaking and grinding equipment cannot be compared directly with graining kettles or the crystallizers, centrifuges, the dryers of the crystallization process, it seems safe to conclude that the smaller equipment needed to handle the relatively small amount of chemical in process means a substantially lower equipment investment for flaking. The same conclusion is reached when a comparison is made with the tower and dryer used in the prilling process. The remaining steps, coating and bagging, are common to other processes.

Table I. Comparison of Different Types of Ammonium Nitrate Products

	Oslo Krystal	Prills	Commercial Solvents Corp. (Stengel)
Screen Analysis, Weight %			
Mesh			
+5	0	0.1	0.1
−5 to +10	0	12.7	75.0
−10 to +14	0.1	76.2	13.9
−14 to +20	23.0	10.0	10.0
−20	76.9	1.0	1.0
Product Analysis			
Nitrogen, %	33.0	33.5	33.5
Bulk density, lb./cu. ft.	72	45–52	56
Moisture, %	0.1	0.2–0.6	0.2–0.4
Coating agent, %	3.0–4.0	2.7–3.5	2.0–3.0

Small Laboratory Reactors Were Used in First Studies

Among the laboratory reactors used in developing the Stengel process were a $^{9}/_{16}$-inch inside diameter tube 3 feet long made of glass and a 1-inch diameter, 42-inch tube of stainless steel. Glass beads were used as packing in both cases. Reactors could be operated either in a vertical or an inclined position. Production rates up to 5 pounds of dry ammonium nitrate per hour were achieved in the $^{9}/_{16}$-inch reactor.

Observation of the hardened material which formed when small quantities of the molten ammonium nitrate were spilled on the laboratory bench led to CSC's selection of a flaking process to convert the liquid nitrate to solid. Considering means by which such a solidification process could be carried out commercially, the investigators hit upon the idea of a metal cooling belt onto which the molten salt could be run at one end and a solid sheet removed at the other. Such belts are in common use in the candy industry and are finding increasing application in the chemical industry. Laboratory studies on a 12-inch belt proved successful and the decision was made to adopt this method.

Flaking, as practiced in this process, is advantageous in that it helps produce particles of the proper size. The finished product, which results from breaking and grinding the sheet, should have a particle size range of −5 to +20 mesh. Smaller particles tend to make the product more susceptible to caking as ammonium nitrate takes up moisture from the air quite easily. The thickness of the sheet can be controlled, and since the crystal orientation of the sheet results in cleavage in a direction perpendicular to the belt, one dimension of each product particle is equivalent to the thickness of the sheet. Even the particles of fines, which are removed and reprocessed, are in the form of needlelike crystals whose length is equivalent to the thickness of the sheet.

Pilot Plant Yielded Design and Operating Data for Large Plant

The pilot plant used in the development of this process has been described (*1*). Each step in the system was evaluated.

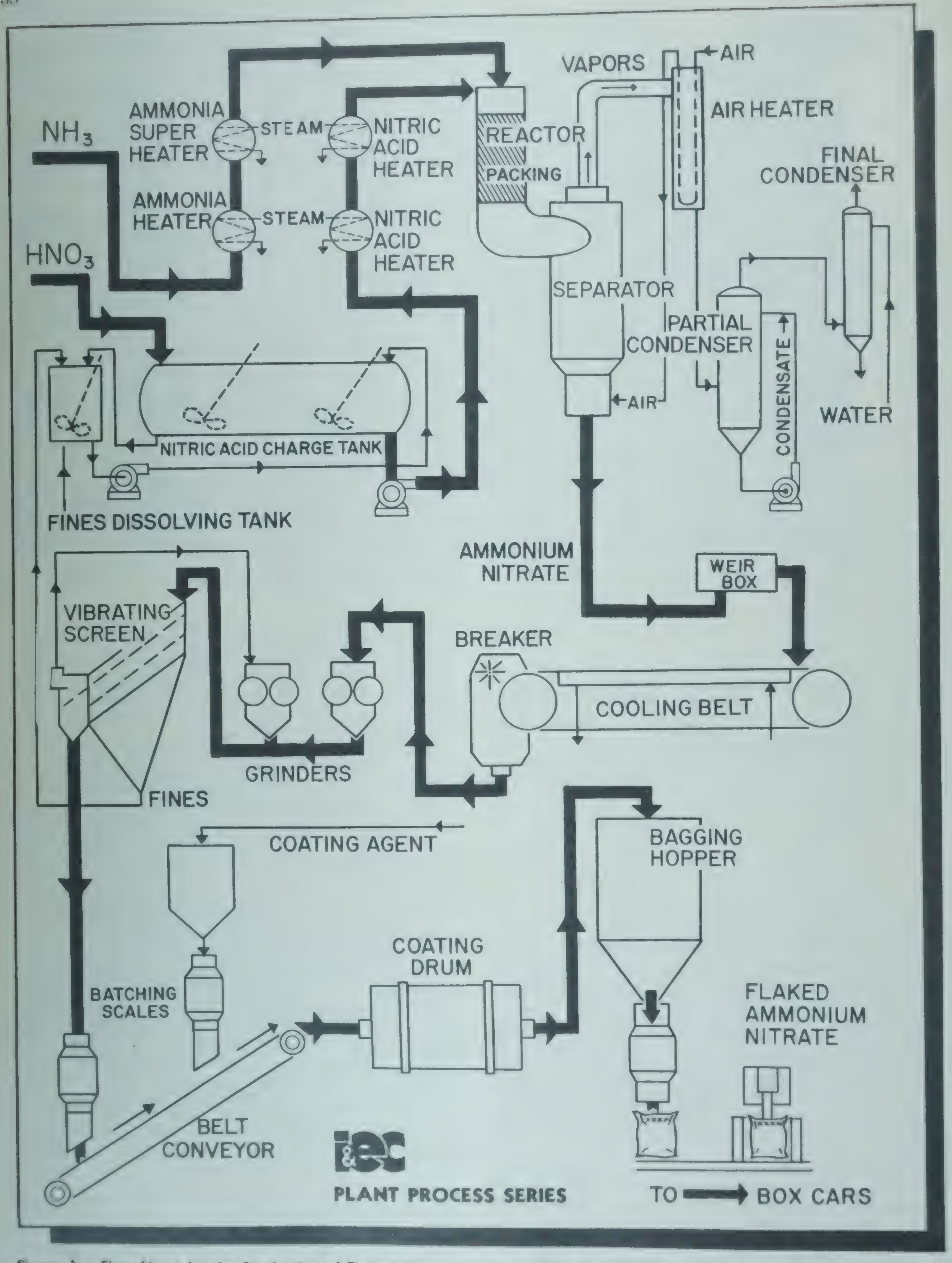

NH$_3$
HNO$_3$
AMMONIA SUPER HEATER
AMMONIA HEATER
STEAM
STEAM
NITRIC ACID HEATER
NITRIC ACID HEATER
REACTOR
PACKING
VAPORS
AIR
AIR HEATER
FINAL CONDENSER
SEPARATOR
PARTIAL CONDENSER
CONDENSATE
AIR
WATER
NITRIC ACID CHARGE TANK
FINES DISSOLVING TANK
AMMONIUM NITRATE
WEIR BOX
VIBRATING SCREEN
BREAKER
COOLING BELT
GRINDERS
FINES
COATING AGENT
BAGGING HOPPER
BATCHING SCALES
COATING DRUM
FLAKED AMMONIUM NITRATE
BELT CONVEYOR
I&EC
PLANT PROCESS SERIES
TO BOX CARS

Figure 1. Flow Sheet for the Production of Flaked Ammonium Nitrate by the Stengel Process at the Sterlington, La., Plant of Commercial Solvents Corp.

The pilot plant reactor was a $2^{1}/_{2}$-inch outside diameter, stainless steel, packed tube, 7 feet tall. One 20-inch wide cooling belt was used. The pilot plant was run for 18 months during 1952 and 1953, closing down with the starting up of the full scale plant in August 1953. It provided invaluable operating data that could be scaled up to the production unit, it was responsible for alteration in the final process design and also served in training some of the operating personnel. Production rates from 600 to 1000 pounds per hour gave sufficient material for testing storage properties and field effectiveness of the product.

The ammonium nitrate plant is part of a $20,000,000 expansion program at Sterlington, La., which Commercial Solvents Corp. started in 1951. The Sterlington plant was originally built and operated by CSC for the Government as the Dixie Ordnance Works during World War II. In 1946 the plant was purchased from the Government and expanded. The methanol process at this plant has been described in another article of this series (*4*). The plant also produces ammonia and nitrogen solutions for fertilizers and has facilities for packaging antifreezes. Ammonia capacity is 400 tons per day. The nitrate plant is located about 5 miles from the older installations.

Anhydrous Ammonia Is Brought to Plant by Tank Car or Pipeline

Liquid anhydrous ammonia arrives at the ammonium nitrate plant from the ammonia plant either through a 4-inch line or by tank car. The pipeline is the preferred route, but tank cars were used during start-up operations and are available for use if needed. Temperature of the ammonia when it arrives at the nitrate plant is 5° to 15° F.

Duplicate ammonia unloading systems are provided for the ammonium nitrate and the nitric acid plants. Two 26,500-gallon carbon steel horizontal charge tanks and a weigh tank of the same size are included in each system. These tanks are 54 feet long, 8 feet 8 inches in diameter, and have hemispherical heads. The system is so arranged that one charge tank will supply ammonia to process while the other is being used to develop ammonia pressure for forcing liquid ammonia from the tank car into the weigh tank. In the weigh tank the ammonia is measured for inventory purposes before it drops into one of the charge tanks.

Each charge tank is equipped with a reboiler type heat exchanger for vaporization. Ammonia flows through the shell side while 150 pounds per square inch of steam is connected to the tube side. Steam pressure is controlled (*4i*) by the vapor pressure of the ammonia in the tank so that constant pressure may be maintained at any desired preset level, ordinarily 150 pounds per square inch. The tank being used to provide the pressure for tank car unloading contains liquid ammonia with a vapor space above it. Ammonia vapor flows from the vapor space to the tank car through the ammonia unloading superheater—which raises the temperature to about 185° F. in order to reduce condensation by the cold (5° to 15° F.) liquid ammonia in the tank car. The pressure in the tank car is thus increased from 15 or 20 pounds per square inch gage to 110 pounds per square inch gage, and liquid ammonia flows from the car into the weigh tank.

After a batch is weighed any pressure difference between the weigh tank and the second charge tank is removed by opening a valve in a line connecting the vapor spaces of the two tanks. Then the load is allowed to flow by gravity into the charge tank. The liquid in the weigh tank is at a temperature of 5° to 15° F., and in dropping into the vapor space of the charge tank it brings about a condensation there which reduces the pressure from the original 150 pounds per square inch to approximately 35 pounds per square inch. The charge tank may be used for car unloading as soon as it has been brought up to 150 pounds per square inch pressure by the vaporizer. The tank is then switched to process, after first balancing to eliminate any sudden change of pressure that would cause fluctuation in the rate of ammonia feeding to process. By the system a 25-ton car of ammonia can be unloaded in an hour. When ammonia from the transmission line is used, it is run directly into the weigh tank.

Plant Has Own Nitric Acid Units

Nitric acid for the process is made at the nitric acid plant located near the site of the ammonium nitrate installation. Ammonia is oxidized in three conventional Du Pont units (*4E*). The acid is transferred from the nitric acid plant to two 71,000-gallon vertical nitric acid storage tanks, 22 feet in diameter and 25 feet tall, through a 3-inch stainless steel line. Most tanks, piping, and other fabricated equipment for handling nitric acid in the ammonium nitrate plant are of Type 304 extra-low carbon (ELC) stainless steel, with the exception of the tantalum heat exchanger which will be discussed later. Flow sheets for the process are shown in Figures 1 and 2. Either of two pumps (*18E*) is used to pump the nitric acid from storage into the nitric acid charge tank through a 2-inch line. A liquid level controller (*7i*) in the charge tank actuates a valve which controls the flow of acid into the charge tank. The charge tank is a 14,100-gallon horizontal tank 8 feet in diameter and 36 feet long.

Nitric acid is pumped to the reactor through the stainless steel nitric acid preheater (*1E*) and the tantalum heater (*7E*) by one of two charge pumps (*14E*) with mechanical seals (*6E*). The preheater is a shell-and-tube type exchanger with the acid flowing through the tubes and 150 pounds per square inch steam on the shell side. The tantalum heater consists of three identical tube bundles in series; the tubes are of tantalum, and the heads are stainless steel lined with tantalum. It is extremely difficult to repair tantalum equipment in the field. By constructing the exchanger so that it consists of the three separate bundles, one bundle may be removed for repairs and replaced by a stainless steel spool. In this way operation, although somewhat reduced, may still continue. The nitric acid from the heater goes directly to the reactor. Rotameter controllers (*6i*) control the nitric acid flow in proportion to the ammonia flow into the reactor.

There are good economic reasons for using two separate heat exchangers for heating the nitric acid. At temperatures under 200° F. nitric acid is not especially corrosive to stainless steel, therefore, this relatively cheap material is very satisfactory in the equipment for raising the temperature from 85° to 175° F. To increase the temperature of the acid from 175° to 290°–320° F. where it would attack stainless steel, the more expensive tantalum exchanger is used.

Ammonia vapor from the charge tanks flows through two heat exchangers before going into the reactor. The purpose of the first exchanger is to bring the ammonia vapor to a constant temperature for accurate metering through a rotameter controller (*6i*). The exchanger is similar to the ammonia unloading superheater. The ammonia superheater brings the temperature up to 290° to 300° F. Both exchangers are horizontal shell, U-tube exchangers with longitudinal, finned tubes. Ammonia flows through the shell side with 150 pounds per square inch steam on the tube side.

Ammonium Nitrate Formed by Reaction of Ammonia and Nitric Acid in Reactor

The reactor (*11E*) has an outside diameter of 16 inches and is 10 feet tall. It is fabricated of $^{1}/_{4}$-inch and $^{3}/_{16}$-inch Type 304 ELC stainless steel and is filled with packing. The construction of the reactor is shown in Figure 3. The nitric acid, which may contain ammonium nitrate from the dissolved fines, is mixed with ammonia vapor in the top of the reactor. The ammonia and nitric acid react to form ammonium nitrate in the reaction

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3 + 20{,}600 \text{ cal.}$$

A very slight excess of ammonia is used. The ammonium nitrate is formed as small molten particles. The reactor packing provides

Two Ammonia Unloading Systems Are Provided

Upper tanks are weigh tanks, and lower ones are charge tanks

Ammonia Is Oxidized to Nitric Acid in Three Conventional Du Pont Units

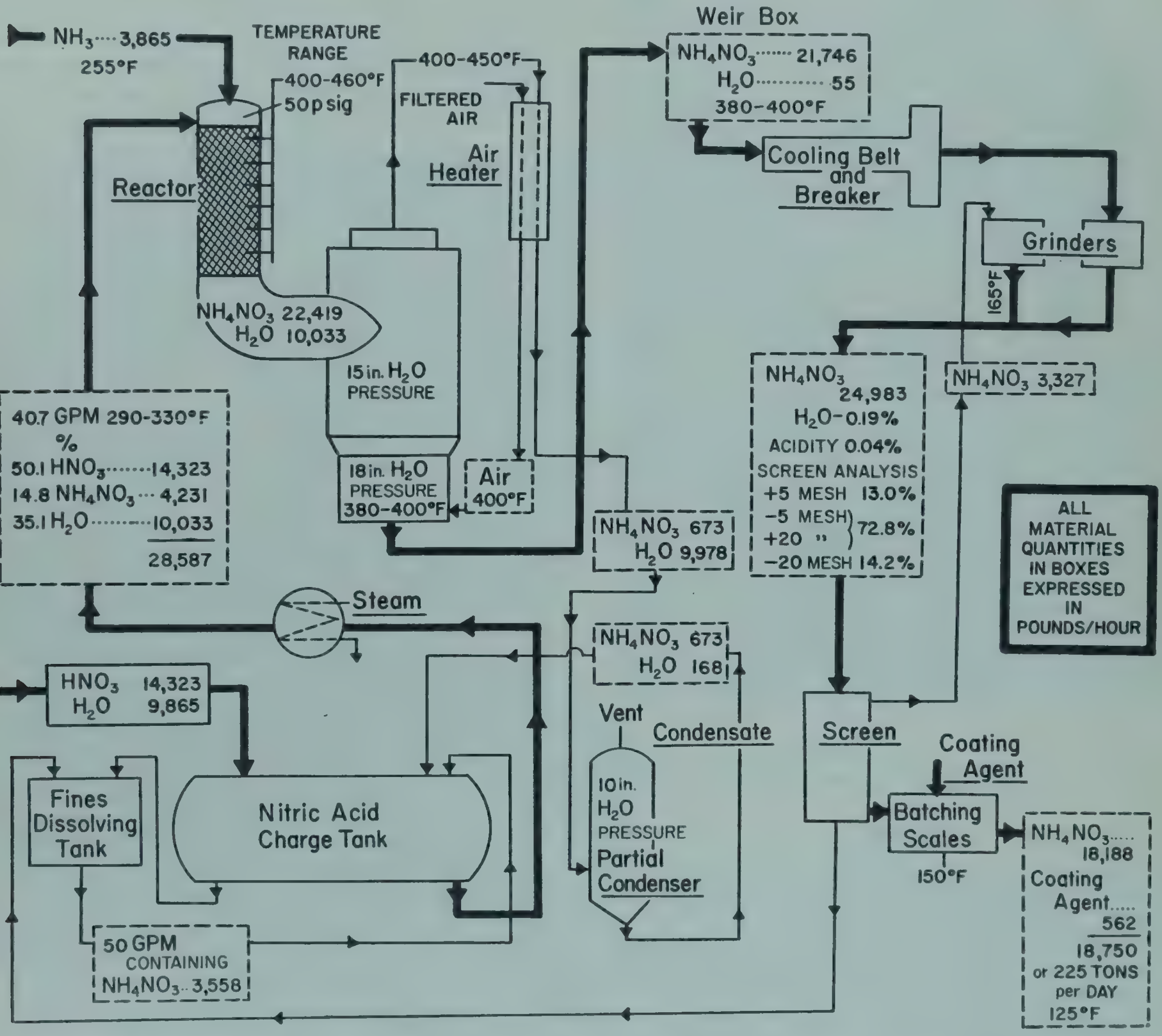
Ammonium Nitrate May Be Recycled to Nitric Acid Charge Tank

Barricade is shown at right

a reaction and condensation surface. Thermocouple readings at different levels of the packing indicate a rise in temperature from about 400° F. at the first thermocouple, about 2 feet below the top of the packing, to about 460° F. at the last one, at the bottom of the packing. The temperature in the reactor is controlled by the temperature to which the nitric acid is preheated. From the reactor, ammonium nitrate, steam, and a trace of ammonia flow to the separator.

Further Processing Removes Traces of Ammonium Nitrate from Vapor

Besides moisture, the air leaving the stripper carries a small amount of entrained ammonium nitrate. Most of this is removed by the entrainment separator (*3E*) from which it drops to the packing. The temperature of the vapor leaving the separator is 380° to 400° F. The vapor conduit from the separator forms



NH₃····3,865
255°F
TEMPERATURE RANGE
400-460°F
50 psig
400-450°F
FILTERED AIR
Air Heater
Reactor
NH₄NO₃ 22,419
H₂O 10,033
15 in. H₂O PRESSURE
18 in. H₂O PRESSURE 380-400°F
Air 400°F
40.7 GPM 290-330°F
%
50.1 HNO₃·······14,323
14.8 NH₄NO₃···4,231
35.1 H₂O·········10,033
28,587
Weir Box
NH₄NO₃······21,746
H₂O··········55
380-400°F
Cooling Belt and Breaker
Grinders
165°F
NH₄NO₃ 24,983
H₂O-0.19%
ACIDITY 0.04%
SCREEN ANALYSIS
+5 MESH 13.0%
-5 MESH
+20 " 72.8%
-20 MESH 14.2%
NH₄NO₃ 3,327
NH₄NO₃ 673
H₂O 9,978
ALL MATERIAL QUANTITIES IN BOXES EXPRESSED IN POUNDS/HOUR
Steam
NH₄NO₃ 673
H₂O 168
HNO₃ 14,323
H₂O 9,865
Vent
Condensate
10 in. H₂O PRESSURE
Partial Condenser
Screen
Coating Agent
Batching Scales
150°F
NH₄NO₃····· 18,188
Coating Agent····· 562
18,750 or 225 TONS per DAY
125°F
Fines Dissolving Tank
Nitric Acid Charge Tank
50 GPM CONTAINING NH₄NO₃··3,558

Figure 2. Materials Flow Sheet Shows Process Stream and Operating Conditions of the Process

The centrifugal portion of the separator collects most of the ammonium nitrate which flows into the packing of the air stripper. The ammonium nitrate flows through the packing to the bottom of the vessel. The temperature of the molten nitrate at this point is approximately 380° to 400° F. Air, heated to 400° F., is blown through the molten salt through two inlets. The air, flowing up through the packing countercurrent to the ammonium nitrate, carries off water vapor, reducing moisture content from about 2.0 to approximately 0.2%. The air is filtered through a packed vessel before heating. It is extremely important that no oil or other extraneous matter be blown into the air stripper since carbonaceous matter causes ammonium nitrate to be more susceptible to explosion. The ammonium nitrate leaving the bottom of the air stripper flows to the weir box. The reactor-separator assembly is so arranged that there is an absolute minimum of liquid material held up in the system.

the shell side of the air heater. A U-tube bundle through which the incoming air flows is inserted directly into the vapor line.

After passing through the air heater, the vapor flows to the partial condenser were the traces of ammonium nitrate and ammonia which it contains are removed. The partial condenser is a conical-bottomed vertical tank, 5 feet in diameter, 12 feet high on the straight side, and packed with Raschig rings. Vapor enters near the bottom and flows upward through the packing. A recirculating pump moves liquid from the bottom of the tank and brings it back into the top where it is distributed over the packing by means of a spray ring. Steam condensate is added to the recirculating solution in amounts controlled by a liquid level controller at the bottom of the condenser. A specific gravity controller (*5i*) in the recirculating line regulates the flow of solution so that when its ammonium nitrate concentration becomes sufficiently high it feeds to the nitric acid charge tank. The vapor passes from the top of the condenser to the bottom of the final condenser, a tank similar to the partial condenser but having no recirculating system. Its purpose is merely to eliminate the nuisance of escaping steam. It is vented to the atmosphere and condensate drains out the bottom.

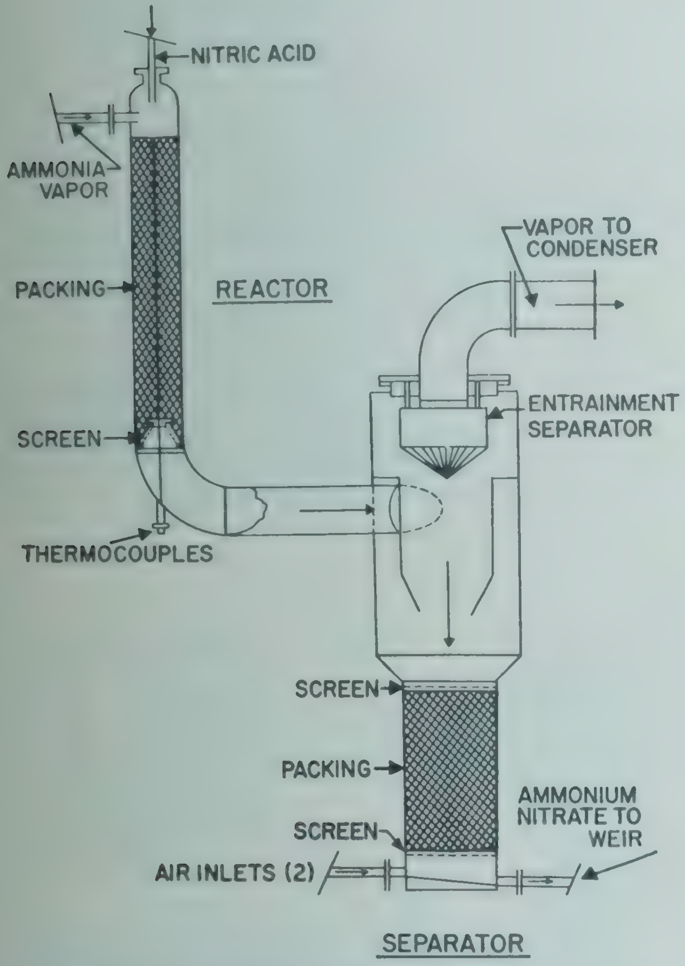


Figure 3. Reactor and Separator Assembly

Molten Ammonium Nitrate Hardens on Cooling Belts

The weir box, constructed of Type 304 ELC stainless steel, divides the stream of molten ammonium nitrate into four equal smaller streams that run through jacketed 2-inch lines to the four continuous stainless steel cooling belts (*15E*). The belts are $31^{1}/_{2}$ inches wide and 0.04-inch thick; with an effective cooling length of 36 feet. Belt speed may be varied between 20 and 100 feet per minute. Three separate aluminum pans containing cooling water are located just under the top half of the belt so that the surface of the water is in contact with the under side of the belt. A fluorocarbon polymer flap presses against the belt near the end receiving the ammonium nitrate and prevents any material from running off the back of the belt. Similar flaps act as guards along the edge of the first few feet of the belt. Hoods made of polymethyl methacrylate panels and aluminum afford protection to the operators from spattering and the fumes, which consist chiefly of steam and minute droplets of ammonium nitrate solution, at the feed end of the belts. During its trip along the cooling belt the salt hardens to form a continuous sheet 24 to 26 inches wide and $^{3}/_{32}$-inch thick. The crystals that form are oriented in a direction perpendicular to the belt. The resulting solid mass will therefore fracture in planes perpendicular to the top and bottom of the sheet.

A doctor blade is set to remove the solid sheet from the surface of the belt; most of the time the sheet is stiff enough so that it flows off the end of the belt of its own accord. At first some difficulties were encountered at the point where the seam in the belt occurred. However, the use of belts welded to form a continuous smooth surface have eliminated this difficulty. At the end of the belt the sheet passes into the sheet breaker (*15E*) which contains a rotating shaft with radiating spokes several inches in length that break the sheet into flakes roughly 2 inches in diameter for more convenient handling.

A conveyor belt system (*9E*), consisting of 8-inch rubber belts with aluminum structure and trough, carries the broken ammonium nitrate to the first grinding station where two hammer-mill type grinders (*8E*) reduces the size of the large flakes. The conveyor belts move the material to the screening operation from which the oversized material is fed to the secondary grinding station where itis subjected to the action of two rotary grinders (*5E*).

Double-Decked Vibrating Screen Achieves Correct Particle Size

A bucket type elevator (*9E*) carries the ground nitrate from the grinder to the vibrating screen (*10E*). The double-decked screen gives a product of 5 to 20 mesh; oversize is sent back to the second grinder while undersize is carried by a screw conveyor to the fines dissolving tank. Particle size could be varied by changing conditions on the cooling belt as well as by changing the grinding and screening operations. The particular size range chosen was selected after trials by the company and consumers. The dissolved fines are pumped to the nitric acid charge tank. Product goes to the batching scale.

Conditioned air is available as required for the vibrating screen and product bin as well as the laboratory and office. Air is conditioned to a constant humidity of 46 grains per pound absolute. The air passes through a unit (*16E*) containing lithium chloride solution kept at a constant temperature and concentration by a steam coil in the air washer and by a regenerator.

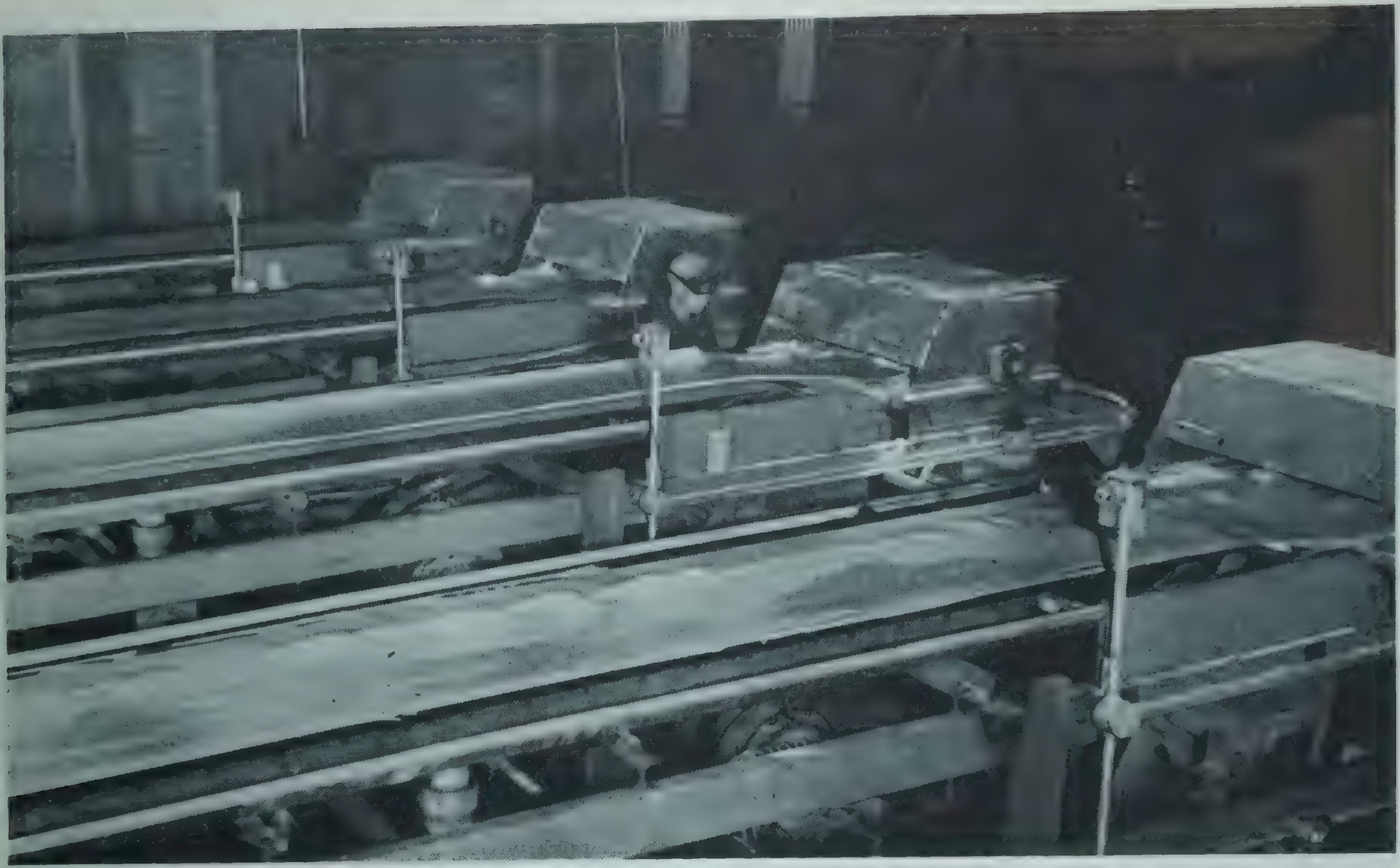
The batching scale (*17E*) automatically discharges 97-pound lots of ammonium nitrate onto an inclined conveyor belt. A second batching scale, interlocked with the ammonium nitrate scale, discharges 3-pound loads of diatomaceous earth which is used as a coating agent. Coating agent is fed to the batching scale from the hopper which is equipped with a paddle-arm agitator and an air agitating system to improve flowability. The conveyor from the batching scales discharges into the coating drum (*12E*). In the rotary coating drum, which is 6 feet in diameter and 20 feet long with internal baffles and mixing flights, the nitrate particles become completely covered with the coating agent which is necessary to prevent caking of the bagged product. A second bucket type elevator (*9E*) carries the product to the bagging hopper where it is discharged through the bagging scale into 100-pound paper bags. A sewing machine (*2E*) with a latex glue and taping mechanism completely seals the bag closure. Temperature of the product in the final stages is at least 20° F. above the ambient temperature. This keeps moisture pickup very low. Even under the most humid conditions, the plant has been able to operate with no reduction in output. Filled bags go by conveyor belt and car loading conveyors (*13E*) directly into box cars. As soon as a box car is filled it is moved down the siding by a small motor truck.

Instrumentation Provides the Precise Control Needed for the Process

The process requires a precise control of the flow and temperature of ammonia and nitric acid which closely approaches a stoichiometric and thermodynamic balance. The raw material input to the reactor is controlled on a ratio basis, the ammonia flow being the independent variable. Area type linear flowmeters (*6i*) on the nitric acid and the ammonia lines are used to transmit

Conveyor Belts Carry Ammonium Nitrate to Grinding Station

Other Belts Carry Material from the Vibrating Screens to Large Rotating Drum (*right*) Where Ammonium Nitrate Particles Are Coated



Four Water-Cooled Stainless Steel Belts Receive Molten Ammonium Nitrate and Discharge a Solid Sheet

a pneumatic signal to a flow ratio controller (*3i*) on a centralizer control panel. The controlled output from this panel is directed to a valve positioner (*1i*) with a characterized cam in its feedback loop. With the proper cam in the valve positioner and the use of this type of flow sensing device, a linear response for all control point settings is ensured.

The nitric acid temperature is maintained constant by two electronic controllers (*2i*)—one on the stainless steel acid preheater and the other on the three-section tantalum exchanger. The ammonia temperature is uncontrolled and is governed by the design of the ammonia heater and its heat transfer characteristics. This is permissible since the heat in the ammonia vapor stream is insignificant in comparison to the total heat in the system.

The safe operation of the process is ensured by two factors, the extremely short residence time and small quantity of material in process and the stability and precision of process control. Any departure from standard operation in either flow or temperature is immediately detected, and proper sequence is automatically established for complete regain of process control.

Plant Start-Up Procedure Takes 0.5 Hour

The ease of starting and stopping the Stengel process is an additional point in its favor. In an emergency, shutdown can be accomplished in a matter of seconds, either manually or automatically. Flow of the reactants is merely cut off and the material in the reactor and separator drains to the belts. Normal shutdown procedure requires 15 minutes. First the nitric acid is shut off and then the ammonia. By shutting off the ammonia after the acid, the reactor-separator system is purged with ammonia so that the equipment contains a noncorrosive atmosphere. If the process is to be closed down for any appreciable period of time the system is washed out with water introduced through the nitric acid line.

The start-up procedure adopted for the plant includes the checking of all mechanical equipment and valves by the operator. He then preheats the reactor and separator assembly to 200° to 210° F. with steam introduced through three inlets—one at the top of the reactor, one in the separator, and one in the stripper. When the desired preheat temperature is reached the steam is cut off and the reactant streams are turned on, the ammonia slightly before the nitric acid. Until the ammonium nitrate leaving the separator reaches normal operating temperature its moisture content is too high, and it is recycled from the weir box back to the nitric acid charge tank. The complete starting procedure requires about half an hour.

Prefabricated Building Houses Portion of Process Not Adapted to Outdoor Operation

The portion of the process best carried out indoors is housed in a prefabricated building 200 feet long, 80 feet wide, with a 20-foot eave height. It is covered with commercial grade 0.032-inch corrugated aluminum. The cooling belts, grinders, screens, batching scales, bagging equipment, and the connecting conveying systems are included inside the building. The control panel is located in a separate room which is part of the building extension which also houses the office and laboratory. It faces a large window which permits the panel to be observed from the factory floor. Placing most of the instruments in a separate room which is pressurized with filtered air helps protect them from the corrosive ammonium nitrate dust. The reactor and weir box are located inside a concrete barricade at the end of the building. The barricade is believed to be unnecessary, but it was included as an extra safety precaution. Likewise a barricade made of wood and filled with earth separates the nitric acid plant from the ammonium nitrate process. All charge tanks, the fines dissolving tank, and the condensers are located outside.

Water requirements for the process are not heavy. Dams were constructed around a nearby lake to impound about 600,000,000 gallons of water. The water is pumped from the reservoir to a settling basin and to the cooling tower basin for the nitric acid plant. In case of fire approximately 170,000 gallons can be pumped from the cooling tower basin and 253,000 gallons from the settling basin. A 1000-gallon-per-minute fire pump developing a 100-pound head feeds the fire protection system. A domestic well furnishes drinking water.

Steam is supplied by a packaged boiler of 30,000 pounds per hour capacity built for pressures up to 250 pounds per square inch gage. It is fired by natural gas. Natural gas is also needed for the primary air compressors in the nitric acid plant.

Industrial waste, consisting mainly of floor washings, is carried into natural drainage facilities by yard ditches fed by trenches, both inside and outside the building. Sanitary wastes are handled by a separate system and flow into a septic tank.

There are twelve warehouses for storing ammonium nitrate. Each building is constructed of steel and is 60 feet wide by 180.5 feet long and approximately 12 feet high. A portable bag conveying system may be moved from one warehouse to another. A room in the plant serves as storage space for coating agent and bags. A 15-day supply of coating agent and a 30-day supply of bags are kept on hand. Larger supplies of coating agent are not kept because it tends to pick up moisture and thereby become less effective if it is stored too long.

Stainless Steel Processing Equipment and Aluminum Structures Prevent Corrosion

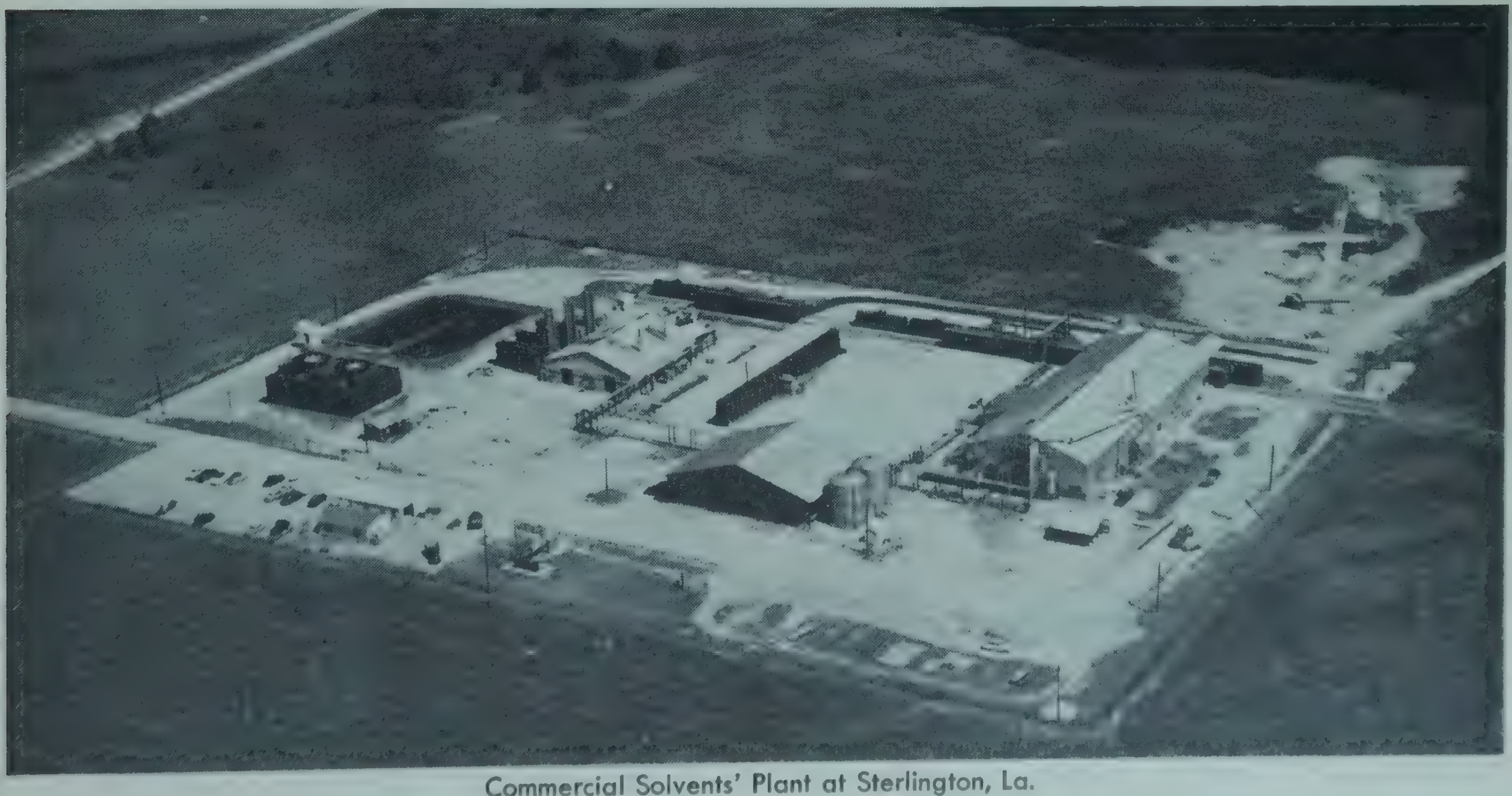
Corrosion presents a serious problem in any ammonium nitrate installation. Processing equipment and lines are generally made of Type 304 ELC stainless steel. Type 347 stainless steel is often used in ammonium nitrate plants, but at the time orders were being placed for the plant it was not available because of government allocations in the interest of national defense. It was decided to use Type 304 ELC (extra low carbon). By specifying "extra low carbon" the difficulty of graining on welding was overcome about as well as it would have been if Type 347 with stabilized carbon were used. Considering the lower price for the Type 304 ELC, it is possible that it should even be the material of choice. As mentioned previously, the nitric acid heater is of tantalum construction. Concrete foundations for the acid pumps and miscellaneous equipment have been shielded with sheet stainless steel so that acid leaks will not corrode them.

Aluminum has been found to be the most economical metal for use around ammonium nitrate. Minute particles of ammonium nitrate dust settle on any exposed surface and then take up moisture to form corrosive solutions. All structural members, housings, nuts and bolts, and other metal parts of the conveying equipment are of aluminum. The main processing building is fabricated of steel with aluminum siding, sash, doors, and trim. Prior to erection, all steel portions of the building were sandblasted and given three coats of special protective paint. One final coat of paint was applied after erection. Even the drainage trenches in the factory floor are lined with aluminum; gratings are of the same metal. The concrete floor is covered with an acid-resistant protective coating. Floors are hosed down at frequent intervals to reduce the contact time of any of the corrosive material which might accumulate.

The electrical system posed a particularly difficult problem in the areas subject to corrosion, because of the need for all-aluminum electrical fittings and devices. Where possible, motor starters and switchgears were located well away from the areas subject to corrosion. Motor starters are of the NEMA Class II oil-immersed type. All conduits, both underground and overhead, are standard aluminum pipe. Fittings are of the cast aluminum threaded cover type. Straps and bolts are also aluminum. No special precautions were taken in connection with conductors since ordinary polyvinyl and neoprene insulations proved to be sufficiently impervious to the corrosive action of the material.

The more serious design difficulties experienced were in connection with motors, control devices, and lighting fixtures placed in the areas subject to corrosion. The basis for selection of each item was governed by how closely it approached all-aluminum or stainless construction. Since most of the items needed were not completely satisfactory it was necessary to make many field modifications such as substitution of stainless or aluminum for many of the brass and carbon steel accessories.

All motors are labeled for Class I and Class II locations and the majority of indoor fittings are explosion-proof or dust-tight, not because of a recognizable code requirement but because of the desire to have extreme ruggedness inherent in explo-



Commercial Solvents' Plant at Sterlington, La.

Ammonium nitrate plant is at right and nitric acid plant at left, beyond barricade; ammonia unloading system is in foreground covered by gabled roof sion-proof equipment in order to further combat the corrosion problem.

Personnel requirements for the plant are small. Each shift is composed of a technical supervisor, one grade V, one grade IV, one grade III, four grade I operators, the higher grade indicating the more skilled operator. During the day there is one laboratory technician and one fork truck operator.

In the laboratory nitrogen determinations are run according to the Official Methods of Analysis of the Association of Official Agricultural Chemists. Specifications call for 33.5% nitrogen. Moisture determination is made by Karl Fischer method; maximum moisture is 0.4%. Since the gravimetric method for determining coating agent is too slow to be used as a rapid control check, the coating agent is routinely determined by dissolving a sample of coated ammonium nitrate in water, and the per cent coating agent is determined by centrifuging. The results obtained by this method are checked periodically by gravimetric analysis. Coating agent runs about 3% by weight of the finished product. Screenings determine particle size distribution. Approximately 1-pound samples are taken from bags at hourly intervals just before they are closed; groups of these samples are then composited for analysis.

Outlook for Ammonium Nitrate Fertilizers Is Good

The outlook for ammonium nitrate is intimately associated with the outlook for ammonia. At the present time 70% of the ammonia produced in this country goes into fertilizers. Demand for ammonia has been very great, and the Government has encouraged expansion of the national capacity by issuing certificates of necessity. The new ammonia plants now coming on stream have resulted in some easing of demand; an indication of this was the Business and Defense Services Administration's action in February of this year discontinuing its program of recommending apportionment of military orders for ammonia among the different producers. The never-ending race between population and food supply is enough to ensure a long term demand for nitrogen bearing chemicals.

Anhydrous ammonia is being used in increasing quantities for fertilizer. At the present time 15% of all nitrogen used as fertilizer in this country goes into the soil as anhydrous ammonia (*3*). The use of anhydrous ammonia is advantageous only under certain conditions (*2*). Its use is limited by soil type, crop requirements, cumbersome application and storage equipment, and other factors. Although anhydrous ammonia undoubtedly will continue to find wider application, total sales of solid nitrogen chemicals are not likely to decline in the near future.

The high nitrogen content of ammonium nitrate and its low cost seem to give it an advantage over other solid nitrogen chemicals. Urea may become more competitive later on but is currently more expensive. There probably will be continuing steady markets for the other solids, but there does not seem to be any possibility of a great growth in their use.

When the ammonium nitrate market becomes more competitive as more plants are built, Commercial Solvents Corp. believes that their economical Stengel process will give them a very good position in the industry.

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(2) *J. Agr. Food Chem.*, **1**, 1141 (1953).
(3) *Ibid.*, p. 1184.
(4) Kastens, M. L., Dudley, J. F., Troeltzsch, J., IND. ENG. CHEM., **40**, 2230 (1948).
(5) Shearon, W. H., Jr., Dunwoody, W. B., *Ibid.*, **45**, 496 (1952).
(6) Stengel, L. A. (to Commercial Solvents Corp.), U. S. Patent 2,568,901 (Sept. 25, 1951).

Processing Equipment

(1E) Armstrong, R. M., Co., West Chester, Pa., vertical shell-and-tube type heat exchanger; tube and head, type 304 ELC stainless steel; mild steel shell with expansion bellows. 6 feet 3 inches long, $10^3/_4$ inches o.d.
(2E) Bagpak Div., International Paper Co., New York, N. Y., sewing machine, Type D-A.
(3E) Centrifix Corp., Cleveland, Ohio, custom-built entrainment separator.
(4E) Chemical and Industrial Corp., Cincinnati, Ohio, nitric acid plant.
(5E) Arthur Colton Co., Detroit, Mich., double rotary granulator No. 544, stainless steel contact parts.
(6E) Durametallic Corp., Kalamazoo, Mich., mechanical seal, glass-filled Teflon against porcelain.
(7E) Fansteel Metallurgical Corp., North Chicago, Ill., heat exchanger, three tube bundles in series, each section 8 feet long, and 9 inches o.d. with tantalum tubes; stainless steel shell with expansion bellows.
(8E) Fitzpatrick, W. J., Co., Chicago, Ill., stationary hammer-type mill, Model D, comminuting machine.
(9E) Link Belt Co., Chicago, Ill., continuous bucket-type elevator, aluminum buckets and housing; conveyor belts.
(10E) *Ibid.*, vibrating screen, Type CA, double deck.
(11E) Littleford Bros., Inc., Cincinnati, Ohio, custom built reactor.
(12E) Louisville Drier Div., General American Transportation Corp., rotating drum, 20 feet long, 6 feet o.d., internal baffles and mixing flights.
(13E) Manierre Engineering & Machinery Co., Milwaukee, Wis., carloader Type V3.
(14E) Peerless Pump Div., Food Machinery & Chemical Corp., Los Angeles, Calif., centrifugal pump, Model DSO-8, 15 hp., 3500 r.p.m.
(15E) Sandvik Steel, Inc., New York, N. Y., custom-made spoke wheel breaker; water bed conveyor.
(16E) Surface Combustion Co., Toledo, Ohio, Kathabar Air Washer No. 1750-27VC: Kathene Regenerator No. 90CB.
(17E) Thayer Steel and Engineering Corp., Rockland, Mass., automatic batching scale, Model 400-N; Model 700 N.
(18E) Wilfley, A. R., & Sons, Denver, Colo., centrifugal pump, Model AF, 5 hp., 1750 r.p.m.

Process Instrumentation

(1i) Bailey Meter Co., Cleveland, Ohio, cam type valve positioner.
(2i) Brown Instruments Div., Minneapolis-Honeywell Regulator Co., Minneapolis, Minn., electronic type thermocouple actuated temperature controller.
(3i) *Ibid.*, flow ratio controller.
(4i) *Ibid.*, pressure controller.
(5i) Fisher Governor Co., Marshalltown, Iowa, bouyancy type temperature compensated density controller.
(6i) Fischer & Porter Co., Hatboro, Pa., steel tube type rotameter transmitter.
(7i) Moore Products Co., Philadelphia, Pa., liquid level controller.

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Modern Portland Cement Production

WILLIAM Q. HULL, *Associate Editor*
in collaboration with
PETER HASS
Permanente Cement Co., Oakland, Calif.
PAUL FRANKLIN
Permanente Cement Co., Permanente, Calif.

PORTLAND cement plays a leading role as a building material in today's civilization. It is considered indispensable in sidewalks, highways, bridges, and dams; in the construction of practically all large buildings; and in dry docks, harbors, and airports. Both country and city dwellers daily use or come in contact with its applications in countless ways. The almost universal use of portland cement can be credited to the comparative ease of working it, its strength (which increases with age), and its uniformity (which makes it possible to calculate strengths as reliable as those made for steel). Its permanency and minimum maintenance contribute to the popularity of its use.

Portland cement's versatility as a material of construction has resulted in a rapid growth of the industry in the United States. In the entire decade beginning in 1870, total production amounted to only 82,000 barrels in the United States. By the turn of the century, annual production had grown to 8,500,000 barrels. In 1950, over 222,000,000 barrels were produced in 150 plants scattered throughout the nation. Table I shows that during this period, the dollar value of production jumped from $246,000 to over $527,000,000. A breakdown of end uses is shown in Table II.

The history of cement goes back much further than its first production in the United States, however. From the time that man first began to build, he sought a material that would bind stones into a solid, formed mass. The Babylonians and Assyrians used clay for this purpose; the Egyptians found blocks bound with lime and gypsum mortar satisfactory in building the Pyramids; the Greeks developed a cement used in structures that showed remarkable durability. The Romans experienced great success in making a cement in which slaked lime was mixed with volcanic ash from Mt. Vesuvius. This material, called *pozzolana*, produced a cement capable of hardening under water and was the first so-called hydraulic cement. Well-known examples of Roman architecture which have lasted through the ages are the Colosseum, the Basilica of Constantine, and the great Roman baths built around 27 B.C.

The secret of cement that would harden under water was lost during the Dark Ages, and from the period of the Romans no advances were made in the technology of building materials until the latter part of the eighteenth century. It was then that the modern cement industry had its beginning. John Smeaton, an English engineer, was employed to build a lighthouse on the rug ged coast off Cornwall where repeated failure had been experienced with wooden structures. Smeaton knew that ordinary lime mortar would not harden under water, and this was a requirement if the foundation of the lighthouse was to be firm. In 1756, he launched a series of investigations which eventually led to a satisfactory material made from the burning of limestone containing a considerable proportion of clay (*13*). The Eddystone lighthouse, which Smeaton built in 1759, stood for 126 years before it had to be replaced. Not only did Smeaton develop a cementitious material for his purpose, but modern lighthouse construction began with his work.

In making his hydraulic lime, Smeaton used only those layers of the quarry which, after calcining, gave a product that would slake with water. It did not occur to him that the layers which would not slake readily could be burned, and, after grinding, could be converted into a good hydraulic lime. Forty years later, Joseph Parker of England was granted a patent for the manufacture of a hydraulic lime which was made by calcining argillocalcareous nodules (calcareous and clay-bearing material) similar in composition to cement rock, and then grinding the resulting clinker into a powder. In 1810, Edgar Dobbs obtained an English patent for the manufacture of an artificial Roman cement by mixing carbonate of lime and clay in suitable proportions, moistening, molding into bricks, and burning sufficiently to drive off the carbonic acid without vitrifying the mixture. Other experimenters in the field of cement during the period from 1756 to 1830 were Vicat and Lesage in France and Parker and Frost in England (*4*).

Joseph Aspdin, a bricklayer of Leeds, England, is usually credited with the invention of "portland" cement. In 1824, he was granted a patent on a hydraulic cement which he called "portland" because it resembled in color the stone from the Isle of Portland off the British coast (*3*). Historians do not give all the credit to Aspdin, however. While he did orginate the name "portland cement," he did nothing more than make an artificial Roman cement, which had been done before. He did not carry his burning to the point of incipient vitrification (30 to 35% liquid phase), which is now recognized as an essential step in the manufacture of portland cement as it is known today (*5, 8, 14*).

Aspdin's greatest contribution was his method of carefully proportioning limestone and clay, pulverizing them, and burning the mixture into clinker which was then ground into finished cement. In contrast to natural cements, produced by burning a naturally occurring mixture of limestone and clay, portland cement is a predetermined and carefully proportioned chemical combination of lime, silica, iron oxide, and alumina. Because the ingredients of natural cement varied widely, the properties of the final product varied just as greatly, and although the natural cement industry was at one time important, over 98% of cement produced in the United States today is portland cement.

The origin and development of the cement industry in the United States has been credited to the sudden and large demand for a good hydraulic cement created by the building of canals, beginning with the Erie Canal in 1817 (*12*). At about this time, large rock deposits were discovered in New York from which natural hydraulic cement could be made with very little processing. By 1890, nearly 10,000,000 barrels of natural cement were being produced annually in the United States and Canada, a large part of which was used in construction of the canal systems. Portland cement began to replace the natural product in England in 1850 and was first manufactured in the United States, in 1870, by the Coplay Cement Co., near Allentown, Pa., an area which has continued to be an important one in the industry. This and other early plants used vertical stationary kilns. It was necessary to cool each kiln after burning, and there was considerable waste of fuel and time. Development of the rotary kiln, beginning in England in 1885 and further developed by Thomas A. Edison and others in the United States, was one of the greatest factors that contributed to the growth of the portland cement industry in this country.

Table I. Portland Cement Industry in the United States (*16*)

Year	No. Active Plants[a]	Production, Thous. Bbl.	Value of Product: Total[b], Thous. Dollars	Value of Product: Av. Mill Price/Bbl.	U. S. per Capita Use
1870–79	...	82	$ 246	$3.00	...
1900	50	8,482	9,281	1.09	...
1910	111	76,550	68,206	0.89	...
1920	117	100,023	202,047	2.02	0.87
1930	163	161,197	228,780	1.44	1.29
1935	150	76,742	113,372	1.51	0.58
1936	149	112,650	170,415	1.51	0.87
1937	150	116,175	168,835	1.48	0.87
1938	151	105,357	153,977	1.45	0.81
1939	149	121,935	180,322	1.47	0.95
1940	151	129,831	189,448	1.46	0.96
1941	154	163,568	245,616	1.47	1.25
1942	153	182,114	281,721	1.52	1.38
1943	151	132,446	197,812	1.56	0.95
1944	149	89,883	148,132	1.59	0.70
1945	142	101,340	170,317	1.62	0.77
1946	150	162,296	288,451	1.72	1.16
1947	148	184,658	351,477	1.89	1.25
1948	148	203,008	438,731	2.17	1.34
1949	148	207,535	467,068	2.29	1.35
1950	145	222,808	527,022	2.35	1.47
1951	153	241,782	601,918	2.57	1.53
1952	154	245,019	630,467	2.55	1.57
1953[c]	155	260,365	...	...	...

[a] All existing plants prior to 1905 included.

[b] Value of product produced through 1929; value of product shipped after 1929.

[c] Preliminary figures.

Table II. Uses of Portland Cement by Classes of Construction (*17*)

(Continental United States in 1949)

	Thous. Barrels	%
Nonresidential building (commercial, industrial, institutional, social, and recreational)	52,810	22.5
Highways (streets, roads, alleys, bridges, sidewalks, and related structures)	35,397	15.1
Residential building (excluding farm dwelling units)	32,016	13.6
Public utilities (railroad, fuel, power, telephone, and telegraph)	23,630	10.1
Military and naval (construction at military establishments—airfields, cantonments, piers)	22,734	9.7
Conservation and development (all work on reclamation, river, harbor, and soil conservation projects)	17,782	7.6
Farm (dwellings and service buildings)	10,950	4.6
Sewer and water (sewage treatment, water supply, and sewerage systems)	9,048	3.8
All other new construction (including civil airports)	4,053	1.7
Maintenance and repair (including work on all classes)	26,003	11.1

The Chemistry of Portland Cement Is Not Fully Understood

The definitions of portland cement and the opinions on what shall be included in the term vary considerably in the standard specifications of different countries. In Great Britain, the official definition is worded:

> The cement shall be manufactured by intimately mixing together calcareous and argillaceous and/or other silica, alumina, or iron oxide bearing materials, burning them at a clinkering temperature, and grinding the resulting clinker so as to produce a cement capable of complying with this specification. No addition of any material shall be made after burning other than calcium sulfate, or water, or both. No cement to which slag has been added or which is a mixture of portland cement and slag shall be deemed to comply with this specification (*9*).

In the United States, the definition is:

> Portland cement is the product obtained by pulverizing clinker consisting essentially of hydraulic calcium silicates to which no additions have been made subsequent to calcination other than water and/or untreated calcium sulfate, except that additions not to exceed 1.0% of other materials may be interground with the clinker at the option of the manufacturer, provided such materials in the amounts indicated have been

In the quarry, a five-cubic yard shovel loads blasted rock into end-dump buggies

After passing through primary crushers, limestone is conveyed to a transfer station which routes it to appropriate high or low carbonate surge piles

Secondary crushing plant is in vicinity of cement plant; rock and clay storage piles are in background

Over-all view of Permanente, Calif., plant shown to be not harmful by test carried out or reviewed by (ASTM) committee on cement (*1*).

France briefs the definition even further and calls portland cement an intimate mixture of carbonate of lime, silica, alumina, and iron burnt to the point of incipient fusion and ground.

Technically portland cement is a greenish-gray. chemically active, impalpable powder made by burning to a high temperature in a rotary kiln a pulverized mixture containing definite proportions of oxides of calcium, silicon, and aluminum and iron, and grinding the resultant clinker. Two to six per cent of gypsum by weight (based on maximum limit of 2.0 to 2.5% SO_3 in the cement) is added during grinding of clinker to control setting time.

The most commonly used portland cements contain the following proportions of mineral oxides:

	Range, %	Average, %
Calcium oxide	60–66	64.0
Silicon dioxide	20–25	22.5
Aluminum oxide	3–8	6.5
Iron oxide	2–6	2.5
Magnesium oxide	0.5–5	2.0
Sulfur trioxide	1–2.5	1.5

Small amounts of sodium, potassium, and traces of other oxides are usually present

In the cement clinker, the elements are not present as the simple oxides shown. Silicon dioxide, aluminum oxide, and iron oxide are inactive under ordinary conditions and have no cementitious characteristics Calcium oxide and magnesium oxide absorb moisture and carbon dioxide from the atmosphere to form hydroxides and carbonates and in this form are valueless as cementitious materials. Calcium oxide alone or mixed with magnesium oxide is converted into the hydroxide by proper application of water and forms a cementitious material but one that does not have the hydraulic characteristics of portland cement (*20*).

The cementitious properties of portland cement are therefore not the result of the presence of the simple oxides but of complex hydraulic calcium silicate compounds formed in the burning operation. The actual compounds present did not interest the early investigators. By trial and error, procedures for selecting raw materials and proportioning and processing them had been developed. Beginning in 1887 with the work of Le Chatelier, who was the first chemist to apply methods employed in petrography to the study of cement, and extending to current work of portland cement scientists, the knowledge of the chemistry of portland cement has been expanded considerably (*11*).

It is now generally agreed that in the calcined clinker the oxides of calcium, silicon, aluminum, and iron are combined to form a mixture of the following compounds:

Tricalcium silicate	$3CaO{\cdot}SiO_2$
Dicalcium silicate	$2CaO{\cdot}SiO_2$
Tricalcium aluminate	$3CaO{\cdot}Al_2O_3$
Tetracalcium aluminoferrite	$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$

For some time, these four compounds have been accepted as the principal compounds of portland cement clinker. (Magnesium oxide is believed to remain in its uncombined state.) More recent work has shown the presence of a new ternary compound, $6CaO{\cdot}2Al_2O_3{\cdot}Fe_2O_3$ and a series of solid solutions extending from $6CaO{\cdot}2Al_2O_3{\cdot}Fe_2O_3$ to $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ (*19*).

The portland cement chemist generally refers to the four important compounds listed as C_3S, C_2S, C_3A, and C_4AF. They are generally present in the five regular types of portland cement in the ranges shown:

	%
C_3S	2.5–65
C_2S	7.0–45
C_3A	2.0–15
C_4AF	6.0–15

While the exact composition of the clinker is not fully understood, increased knowledge is a result of mathematical analysis, physical chemistry, petrography, x-rays, and use of the electron microscope.

The four principal compounds are unstable and when wetted rearrange with different speeds. C_3A reacts with great rapidity, generating the greatest amount of heat, and contributes to the initial set of the cement. C_3S also reacts rapidly forming gelatinous silica and calcium hydrate, and contributes to the early strength of the concrete. The reactions continue until the gelatinous material has bound the grains of sand and crushed stone used in concrete into a hard mass. C_2S hydrates slowly over a long period of time and contributes to the later strength of concrete. Hardening continues for years, and the strength of concrete increases with time. After several years, an additional element of strength is a result of crystallization of the gelatinous calcium hydrate.

The hydration of cement is a complex process, however, and the reactions that occur when cement is mixed with water are far from fully understood. Bogue and Lerch have observed the following reactions and hydration products when working with each of the compounds separately (*7*):

1. C_3S forms crystalline calcium hydroxide and an amorphous calcium silicate of composition approaching $2CaO{\cdot}SiO_2{\cdot}XH_2O$.
2. Compounds containing alumina react to form a fluffy, crystalline, isotropic, hydrated calcium aluminate of a composition $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$.
3. C_4AF forms an amorphous hydrate, the composition of which has not definitely been established, and crystalline $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$.
4. Gypsum reacts with the alumina that enters into solution to form crystalline calcium sulfoaluminate, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$.

Generally, it is considered that magnesia does not react, and its presence is limited to 4% by weight in the cement according to type of cement. When present in amounts greater than this, it contributes to unsoundness of the concrete.

In practice, the percentage of each of the compounds present is determined generally from calculations based on oxide analysis. The relationships are:

$$C_3S = (4.07 \times \%\ CaO) - (7.60 \times \%\ SiO_2) - (6.72 \times \%\ Al_2O_3) - (1.43 \times \%\ Fe_2O_3) - (2.85 \times \%\ SO_3)$$

$$C_2S = (2.87 \times \%\ SiO_2) - (0.754 \times \%\ C_3S)$$

$$C_3A = (2.65 \times \%\ Al_2O_3) - (1.69 \times \%\ Fe_2O_3)$$

$$C_4AF = (3.04 \times \%\ Fe_2O_3)$$

The American Society for Testing Materials has specifications for five types of portland cement. These are:

Type I for use in general concrete construction when the special properties specified for Types II, III, IV, and V are not required.

Type II for use in general concrete construction exposed to moderate sulfate action or where moderate heat of hydration is required as in semimassive concrete projects.

Type III for use when high early strength is required.

Type IV for use when a low heat of hydration is required, as in massive concrete dam construction.

Type V for use when high sulfate resistance is required, as in sewage disposal plants, or concrete exposed to severe alkali conditions.

The chemical and physical requirements for the five types are shown in Table III.

The fineness of the final cement product is of great importance. Portland cement tests 95 to 99% through a 200-mesh screen and 88 to 93% through a 325-mesh screen. The fineness expressed in specific surface area or the surface in square centimeters of one gram of cement has become common in recent years.

Lime and silica make up between 70 and 85% of the mass of portland cement. Limestone, shell and chalk or marl combined with shale, clay, slate, or blast furnace slag, are the principal raw materials from which it is made (Table IV). Two processes are used in manufacture, wet process and dry process. When rock is the principal raw material used, primary crushing is the first step

Table III. Portland Cement Specifications (2)

	Type I	Type II	Type III	Type IV[a]	Type V[a]
Chemical Requirements					
Silicon dioxide (SiO_2), min., %	...	21.0	...	...	...
Aluminum oxide (Al_2O_3), max., %	...	6.0	...	...	[b]
Ferric oxide (Fe_2O_3), max., %	...	6.0	...	6.5	[b]
Magnesium oxide (MgO), max., %	5.0	5.0	5.0	5.0	4.0
Sulfur trioxide (SO_3), max., %	2.0[c]	2.0	2.0[d]	2.0	2.0
Loss on ignition, max., %	3.0	3.0	3.0	3.0	3.0
Insoluble residue, max., %	0.75	0.75	0.75	0.75	0.75
Tricalcium silicate ($3CaO \cdot SiO_2$), max., %	...	50	...	35	50
Dicalcium silicate ($2CaO \cdot SiO_2$), min., %	...	...	...	40	...
Tricalcium aluminate ($3CaO \cdot Al_2O_3$), max., %	...	8	15	7	5
Physical Requirements					
Fineness, specific surface, sq. cm./gram					
Average value, min.	1600	1700	...	1800	1800
Min. value of any one sample	1500	1600	...	1700	1700
Soundness					
Autoclave expansion, max., %	0.50	0.50	0.50	0.50	0.50
Time of setting (alternate methods)					
Gilmore test					
Initial set (min.), minutes	60	60	60	60	60
Final set (max.), hours	10	10	10	10	10
Victat test					
Initial set (min.), minutes	45	45	45	45	45
Final set (max.), hours	10	10	10	10	10
Compressive strength (min.), lb./sq. inch					
Test cubes kept					
1 day in moist air	...	...	1250	...	...
1 day in moist air, 2 days in water	900	750	2500	...	...
1 day in moist air, 6 days in water	1800	1500	...	800	1500
1 day in moist air, 27 days in water	3000	3000	...	2000	3000
Tensile strength (min.), lb./sq. inch					
Test briquets kept:					
1 day in moist air	...	...	275	...	...
1 day in moist air, 2 days in water	150	125	375	...	...
1 day in moist air, 6 days in water	275	250	...	175	250
1 day in moist air, 27 days in water	350	325	...	300	325

[a] Types not generally carried in stock.

[b] C_3A content shall not exceed 5% and the C_4AF plus twice the amount of C_3A shall not exceed 20%.

[c] Maximum limit for SO_3 content of Type I cement shall be 2.5% when the C_3A is over 8%.

[d] Maximum limit for SO_3 content of Type III cement shall be 3.0% when the C_3A is over 8%.

in both. In the wet process, after proper proportioning, raw materials are ground, mixed, and charged to the kiln in a slurry. In the dry process, no water is added and the ground, mixed raw materials are charged to the kiln in a dry state. The balance of the two processes is essentially the same. After calcination at approximately 2700° F. in rotary kilns, the clinker is cooled, stored, ground, and shipped.

Table IV. Materials Used in Portland Cement Manufacture—1950 (18)

Total cement produced, bbl.		226,025,849
Average raw materials/bbl. cement, lb.		653
Materials Used		Short Tons
Cement rock		12,981,679
Limestone and oyster shells		49,035,439
Marl		640,462
Clay and shale		7,169,015
Blast-furnace slag		971,125
Gypsum		1,660,461
Sand and sandstone		769,806
Iron materials		379,637
Other materials (diatomite, fluorspar, pumicite, flue dust, pitch, red mud and rock, hydrated lime, tufs, cinders, calcium chloride, sludge, grinding aids, and air-entraining compounds)		148,290
Total		73,755,919
Fuels consumed, 1951	Total	Av./Bbl. Cement
Coal	8,524,719 tons	114.6 lb.
Oil	266,797,104 gal.	8.66 gal.
Gas	102,740,236 thous. cu. ft.	1437 cu. ft.

There are several modifications to the two processes. In a semidry process, only a small amount of water is added, forming pellets or nodules containing approximately 10 to 12% moisture which are charged to the kiln. In a semiwet process, the finished slurry is partly dewatered by filtration, and the filter cake is fed to the kiln. A few American plants use a special process for beneficiation of raw materials, an adaptation of the flotation process common in the mining industry. Approximately 60% of all U. S. and Canadian plants use the wet process.

Permanente Cement Co. Operates Largest Cement Plant in the West

In 1939, Permanente Cement Co. was awarded a contract to supply cement for construction of Shasta Dam, world's greatest overflow dam and a part of California's Central Valley Project. At that time, the company had no existing plant facilities. Construction was begun in June of that year of a two-kiln plant at Permanente, in the western foothills of Santa Clara County near San Jose, Calif. The plant was in production before the end of the year and eventually supplied nearly 7,000,000 barrels of cement for Shasta Dam.

Several expansions followed, and in 1951 a fifth kiln was added to the plant increasing the annual production to 7,000,000 barrels (28,000,000 sacks). The plant is the largest in the West and one of the two largest individual plants in the world.

In addition to the producing plants at Permanente, the company has distributing facilities in Seattle, Wash., Portland, Ore., Long Beach, Calif., Honolulu, T. H., and Anchorage and Fairbanks, Alas. There are three wholly owned subsidiaries: Kaiser Gypsum Co., Inc., with plants at Long Beach and Redwood City, Calif., and a plant under construction in Seattle; Glacier Sand & Gravel Co., in Steilacoom and Seattle, Wash.; and Permanente Steamship Co. The latter operates two self-unloading bulk carrier steamships, the *S. S. Permanente Silverbow* (58,000 barrels) and *S. S. Permanentecement* (40,000 barrels), which supply the distribution points from docks in Redwood City. In Seattle, cement is loaded into converted, self-unloading LST's (19,000 barrels each) which take it to Anchorage; from Portland, converted LSM's (4000 to 5000 barrels each) take cement to dam and other construction sites along the Columbia River.

Permanente's indicated limestone reserves are sufficient for many years of plant operation. An exploratory drilling program is "proving" these reserves several years in advance of need. The quarry is located approximately one and one half miles from the plant. Average year round carbonate content of rock is controlled at 81.5 to 82.5%. This is considerably lower than in most cement plant quarries, where carbonate runs from 85 to 97%, requiring higher percentages of blending materials. Rock is relatively high in silica and low in iron and aluminum. Average rock analysis (ignited basis) is:

	Per Cent
Silica	24.60
Ferric oxide	0.78
Alumina	1.22
Calcium oxide	72.74
Magnesium oxide	0.47
Alkalies	0.19
Ignition loss	36.46

Operations in the quarry proper consist of drilling, blasting, loading, and transporting. To date, no stripping has been necessary in quarrying limestone. In some cases, overburden exists as clay deposits, but this is generally of such composition that it can be used in the mix. An electric, rotary drill, which uses compressed air for removing cuttings, sinks a series (2 to 14) of $7^3/_8$-inch blasting holes ranging in depth from 60 to 125 feet (*10E*). Each hole requires approximately 4 hours of drilling time and holds a charge of 800 pounds of 48% bulk strength blasting powder in cartridges. Approximately 7 tons of rock is collapsed per pound of powder. In many quarries, churn-type drills are used. These are considerably slower, and during their earlier use by Perman-

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ente, yield per pound of powder averaged only 4 tons of rock. As a result of the chemical composition and geological formation in this quarry, rock breaks finely during primary blasting, and very little secondary shooting is required.

A 5-cubic yard shovel loads the rock into end-dump buggies which hold 23 tons (three dippers) per load (*4E, 11E, 29E*). There are five of these buggies, each of which is pulled by tractor power units (*5E*). Average rock quarry capacity is 1000 tons per hour. The buggies discharge the rock to a scalping grizzly with a 6-inch spacing between bars. Formation is such that a high percentage of rock passes through the grizzly.

Crusher facilities include two primary crushers and a group of three secondary crushers. Oversized rock from the scalper flows to a constant-speed jaw crusher (56 × 72 inch set at 10 inches) located below (*3E*). Discharge joins scalper fines and passes over a 48-inch by 72-foot conveyor to transfer station. From this point, it is routed to limestone surge pile over a 48-inch by 135-foot conveyor boom. Equipment to this point can also be used to process low grade rock. In this case, the transfer station serves as a means of routing low grade rock to a separate surge pile. Limestone surge pile has a normal capacity of 10,000 tons. (A second primary jaw crusher has just been added simultaneously with the opening of a new quarry face.)

Clay is secured either as overburden from rock quarry or from clay deposits near the quarry. Up to 1000 tons of clay can be removed per hour. Clay is fairly high in silica content and has following typical analysis (unignited basis):

	Per Cent
SiO_2	42.20
Fe_2O_3	8.50
Al_2O_3	12.38
CaO	14.54
MgO	4.18
Trace compounds	3.36
Ignition loss	14.84

Under the surge pile is a concrete tunnel where rock or clay is fed through manually operated gates to a conveyor. The 42-inch by 520-foot conveyor takes the rock (or clay) to a 3-inch scalping screen. Oversized rock goes to a gyratory crusher which operates at 880 revolutions per minute and delivers approximately 250 tons per hour of minus $3^1/_2$-inch product (*21E*). Rock going through the screen by-passes crusher and is fed to crusher discharge. Combined primary crusher plant rock (or clay) passes over a 48-inch by 4300-foot conveyor through a mountain side to a second transfer station in close vicinity to the cement plant.

Permanente enjoys a distinct advantage in having the quarry located such a short distance from the plant. In many cases, quarry and plant are from several to many miles apart, requiring haulage by truck or rail rather than conveyor.

At the transfer station, rock (or clay) passes by booms to one of three outdoor storage piles: high grade rock (84 to 97% carbonate) goes to a high grade rock storage pile, where normally about 97,200 tons is available; clay goes to a 5000-ton clay storage pile; low grade limestone (79 to 83% carbonate) is conveyed to a 550,000-ton storage pile.

In addition to limestone and quarry clay (which represent approximately 92% of raw materials), Permanente uses laterite clay and small amounts of iron in form of pyrites cinders in production of portland cement (Figure 1). These produce an easier burning blended slurry. Iron is purchased in a form suitable to introduce in raw grinding department. Laterite, a high aluminum, low silica clay, is secured from deposits in Ione, Calif., and is also introduced in raw grind department. Its typical composition (unignited basis) is:

	Per Cent
SiO_2	30.60
Fe_2O_3	20.87
Al_2O_3	24.17
CaO	8.32
MgO	0.71
Ignition loss	15.01

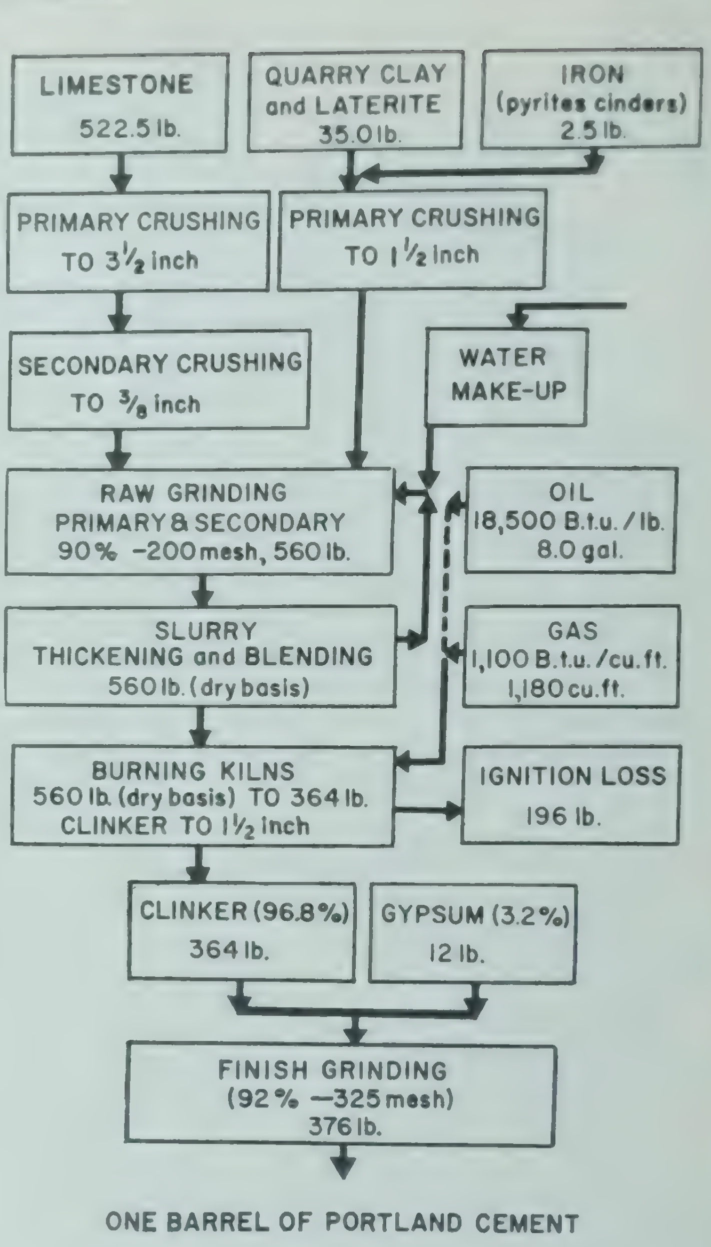


Figure 1. Raw Materials Used in the Production of One Barrel of Portland Cement

Pozzolan cement, used for applications alternately subjected to wetting and drying and to control reactive aggregates, contains approximately 15% of reactive siliceous material added just before milling of clinker. Pozzolan material in itself has no hydraulic properties but reacts rapidly with lime released during cement hydration to give a more durable product when used in concrete. A reactive shale is used commonly for the additive. Pozzolan cement represents approximately 5% of Permanente's annual production.

Rock Is Further Reduced in Size in Secondary Crushing Plant

Crushed rock from primary crushing plant has seen only the beginning of its reduction in size—eventually 90% of it must pass through a 200-mesh screen. Next size reduction occurs in secondary crushing plant. Rock from high and low grade storage piles is blended in ratio of 1 to 3 in secondary crushing plant to maintain average of 82 to 82.5% carbonate content. From either of these piles it is drawn down to conveyors which feed to a 5 × 8 foot double-deck vibrating screen (1-inch opening in top, $^3/_8$-inch slotted bottom). Fines pass directly to cement rock storage pile. Oversized rock passes to a 4-foot standard cone crusher set at $1^1/_2$ inches (capacity of 177 tons per hour) (*12E*). Discharge passes to one of two 5 × 12 foot by $^3/_8$-inch slotted screens. Fines pass to storage and oversized rock to one of two

Table V. Primary Raw Grinding Circuits

Circuit	Equip. Ref.	Ball Mills Diameter Feet	Ball Mills Diameter Inches	Ball Mills Length Feet	Ball Mills Length Inches	Ball Mills Hp.	Rake Classifiers Width, Feet	Rake Classifiers Hp.	Equip. Ref.	Tube Mills Diameter Feet	Tube Mills Diameter Inches	Tube Mills Length Feet	Tube Mills Length Inches	Tube Mills Hp.
							Closed							
1	(*1E*)	9	6	10	0	500	14	40	...	..	..	..	..	..
2	(*16E*)	9	0	11	6	500	12	30	...	..	..	..	..	..
3	(*23E*)	9	6	10	0	500	12	30	(*24E*) (*17E*)	7 7	0 0	26 26	0 0	500 500
							Open							
4	(*16E*)	9	6	13	$2^1/_2$	500	..	..	(*17E*)	8	0	39	$4^1/_2$	1000

$5^1/_2$-foot short-head cone crushers set at $^3/_8$ inches. Each has a capacity of 100 tons per hour and the two are close-circuited on themselves (*13E*). Combined product from the secondary crushing plant is 100% minus $^1/_2$ inch and 90% minus $^3/_8$ inch at a rate of 310 tons per hour. It is conveyed to a 5000-ton surge pile from which it is conveyed to one of three raw storage bins with capacities of 300 and 400 tons each.

Permanente Uses the Wet-Process in Production of Cement

Before calcination, the raw material must be further reduced in size. This is accomplished in the raw grinding department, which is further divided into primary and secondary operations (Figure 2).

Equipment in the primary grinding department is shown in Table V. Three of the four primary raw grinding circuits are operated in closed and one in open circuit operation. The open circuit (No. 4) was added during the last expansion program and was a result of insufficient thickening capacity. In this circuit, raw rock is introduced to a ball mill with sufficient water to make a 30 to 35% slurry (by weight). The ball mill is operated in open circuit with a 39-foot tube mill. Discharge (90% minus 200 mesh, 68 to 70% solids) is sufficiently fine to bypass thickening equipment used in processing discharge from other circuits and is pumped directly to the slurry blending department.

Two of the remaining three circuits (Nos. 1 and 2) are used entirely for rock grinding. Rock is fed to ball mills and water added at same rate. Discharge passes to a 16-foot rake classifier (*6E*). Fines (35 to 40% minus 200 mesh) pass directly to launders or troughs and are pumped to bowl classifiers, and tailings (plus 8 mesh) are recirculated. In grinding clay and iron, material is first passed through a hammer mill which reduces the particle size to a maximum of $1^1/_2$ inches. It then passes to the third of the three closed circuit grinding systems (No. 3). Fines from the rake classifier pass to three hummer screens operated in parallel and in closed circuit with the ball mill. Fines from these screens (minus 14 mesh) are pumped to two 7 × 26 foot tube mills. Discharge from the mills goes to blending tanks.

There are four secondary ball mills. Each is 9 feet 6 inches in diameter and 10 feet long and is operated by a 500-hp. motor (*1E, 16E, 23E*). These are operated in closed circuit with 28-foot bowl classifiers and 16 × 42 foot rakes. In the secondary grinding system, there is a 150 to 250% circulating load. Overflow from the bowl classifiers (14 to 18% solids, 88 to 92% minus 200 mesh) is pumped to one of three outside thickeners. Two are 150 feet in diameter and 10 feet deep (at wall) and the third is 125 feet in diameter and 11 feet deep. Freeboard ranges from 10 to 20 inches. Overflow, which is fairly clear water (less than 1% solids) is pumped to a settling pond. Water from the settling pond is re-used with fresh water. A solids content of 62 to 64% is desirable in thickener underflow. When this is maintained, underflow is pumped directly to slurry blend tanks. When solids content of underflow falls below 61%, a portion of it is pumped to a battery of three 8 × 30 foot rotary filters (*14E*). Filter cake, containing 82% solids, is remixed with balance of slurry to raise per cent solids to desired levels. Filtrate is returned to the thickeners.

Proper Proportioning of Raw Materials Is Made in Slurry Blending Department

In the slurry blending department there are eight tanks of 16,000 cubic feet each and one of 30,000 cubic feet capacity. These are used for unblended slurries of primary clay, iron, and laterite and blends of these with limestone slurry.

Proportioning of the raw materials occurs at this point. From chemical analysis and calculations, correct volumes from each tank are pumped to a slurry blend tank. The slurry blend is thoroughly mixed and pumped to a kiln feed tank.

A typical blending procedure is as follows:

> A blend tank is filled with at least 12,500 cubic feet of raw limestone slurry. To this is added approximately 250 cubic feet of quarry clay, 250 cubic feet of laterite clay, and 100 cubic feet of iron slurry. The tank is agitated with air (30 pounds per square inch) for 10 to 30 minutes. It is analyzed and, if satisfactory, is pumped to kiln feed tank. Here both air and mechanical agitation are provided. Air is introduced through nozzles mounted on the rotating agitator. Holes are protected with a sleeve of artificial rubber which permits compressed air to pass through but prevents slurry from clogging holes.

The blended slurry is now ready to be "burned." During clinkering, the series of chemical compounds making up portland cement are synthesized. Clinkering takes place in a rotary kiln when sufficient heat is supplied to properly proportioned blend of raw materials. The cement industry has been responsible for the growth in size of the rotary kiln from an average common diameter of 5 to 12 feet and from lengths of 25 to over 400 feet.

Some of the largest kilns in the cement industry are the five at Permanente's plant, which are approximately 450 feet long with diameters of 12 feet (Table VI). The kilns are inclined at $^1/_2$ inch per foot of length. Burning zones are lined with a 9-inch layer of periclase-chrome (basic magnesite) burned refractory brick from Kaiser's plant at Moss Landing, Calif. Balance of the kiln is lined with 9-inch and 6-inch high alumina refractory brick (alumina content ranging from 70 to 40%). Normally, natural gas purchased from the local utility (948,000 cubic feet per hour) is used. During extremely cold weather, Bunker C fuel oil (6600 gallons per hour) is used (1 to 2 months a year).

Table VI. Kiln Data

Kiln	Dimensions Ends Feet	Dimensions Ends Inches	Dimensions Center sections Feet	Dimensions Center sections Inches	Length, feet	Normal Speed, R.P.M.	Capacity, Bbl./Day	Equip. Ref.
1	12	2	11	2	454	57	3850	(*19E*)
2	12	2	11	2	454	57	3850	(*19E*)
3	12	0	12	0	444	60	3850	(*26E*)
4	12	2	11	2	454	64	3850	(*19E*)
5	12	2	12	2	448	70	4600	(*19E*)

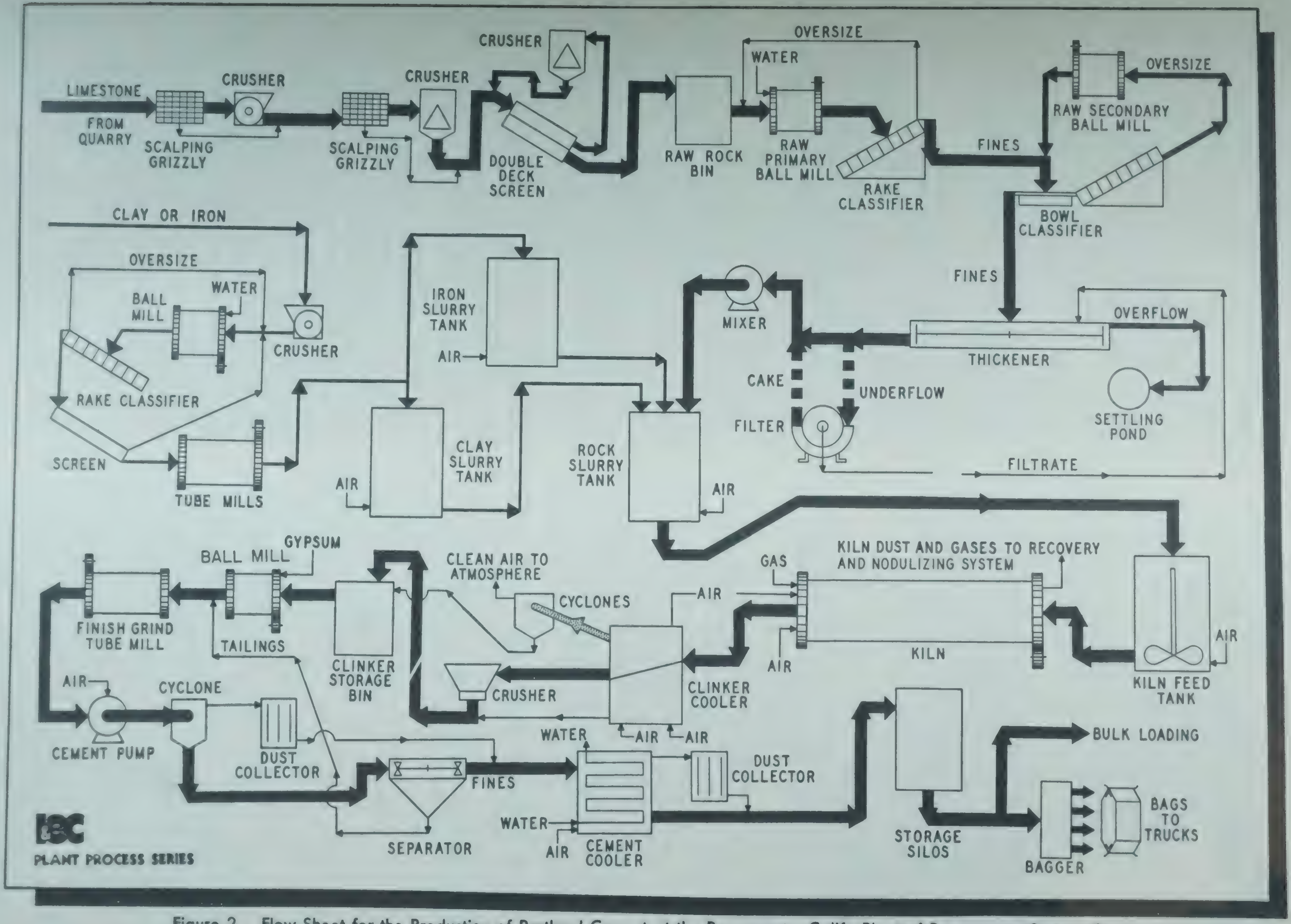
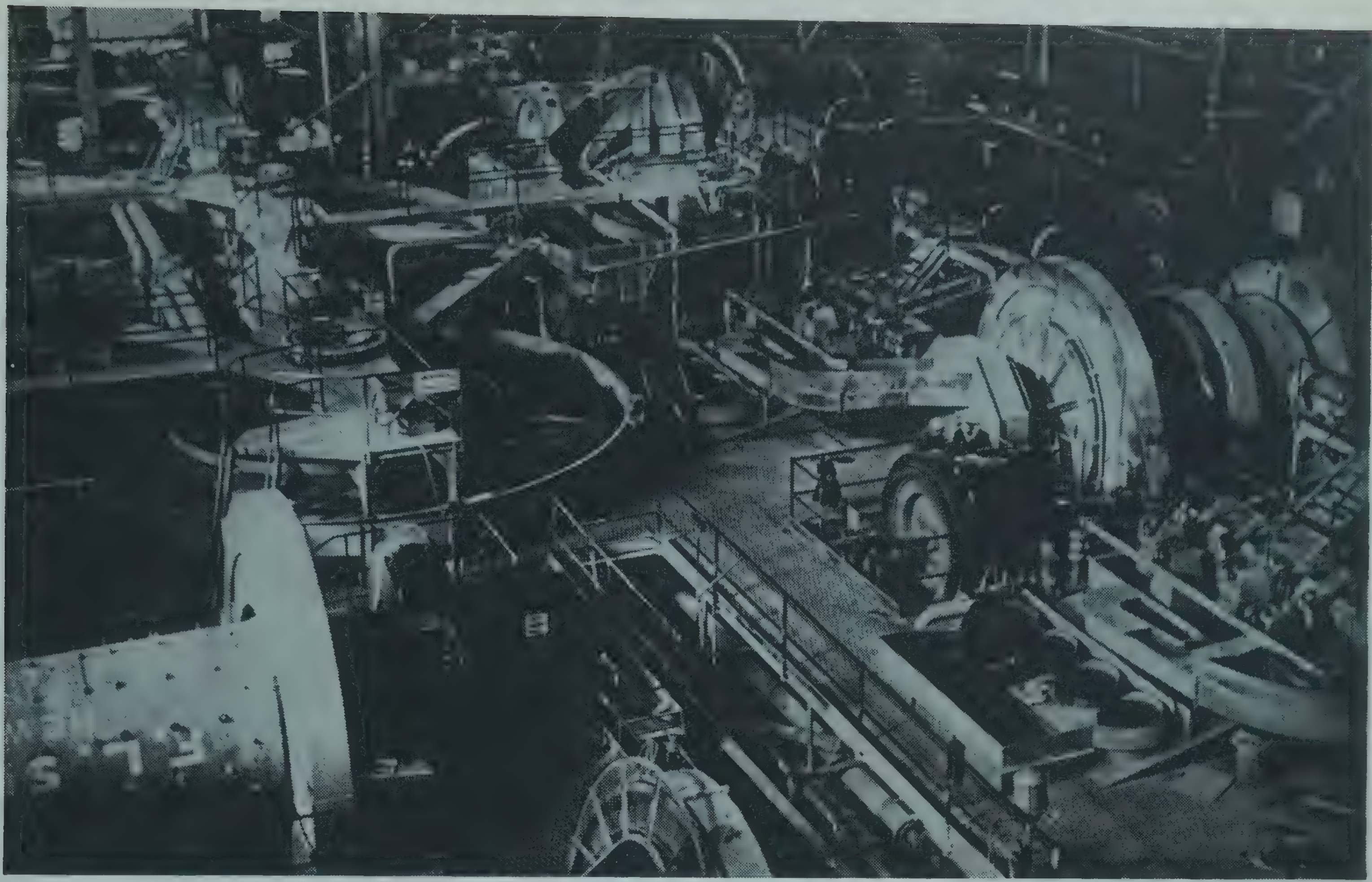

LIMESTONE
FROM QUARRY
SCALPING GRIZZLY
CRUSHER
SCALPING GRIZZLY
CRUSHER
CRUSHER
DOUBLE DECK SCREEN
RAW ROCK BIN
WATER
OVERSIZE
RAW PRIMARY BALL MILL
RAKE CLASSIFIER
FINES
RAW SECONDARY BALL MILL
OVERSIZE
BOWL CLASSIFIER
FINES
CLAY OR IRON
OVERSIZE
WATER
BALL MILL
CRUSHER
RAKE CLASSIFIER
SCREEN
TUBE MILLS
IRON SLURRY TANK
AIR
CLAY SLURRY TANK
AIR
ROCK SLURRY TANK
AIR
MIXER
CAKE
FILTER
UNDERFLOW
THICKENER
OVERFLOW
SETTLING POND
FILTRATE
GYPSUM
BALL MILL
FINISH GRIND TUBE MILL
TAILINGS
CLINKER STORAGE BIN
CLEAN AIR TO ATMOSPHERE
CYCLONES
CRUSHER
CLINKER COOLER
AIR
AIR
AIR
GAS
AIR
KILN DUST AND GASES TO RECOVERY AND NODULIZING SYSTEM
KILN
AIR
KILN FEED TANK
AIR
AIR
CYCLONE
CEMENT PUMP
DUST COLLECTOR
SEPARATOR
FINES
WATER
WATER
AIR
CEMENT COOLER
DUST COLLECTOR
STORAGE SILOS
BULK LOADING
BAGGER
BAGS TO TRUCKS
I&EC
PLANT PROCESS SERIES

Figure 2. Flow Sheet for the Production of Portland Cement at the Permanente, Calif., Plant of Permanente Cement Co.



Raw Grinding Department in Mill Building

Ball mills in closed circuit with rake and bowl classifiers permit accurate control of fineness of raw slurry

The slurry is fed to the kilns through a gravity flow feed pipe by a rotating disk-type feeder which is synchronized with speed of kiln rotation. Overflow from the feeder (5 to 10%) is delivered back to the kiln feed tanks by gravity flow. Fuel is admitted by the burner which extends 8 feet from hood into discharge end of kiln. Burning zone begins approximately 15 feet from hood and is approximately 50 feet long. In this zone, the temperature reaches 2900° F. and the majority of the kiln reactions occur. Primary air is provided by 75-hp. fans. A chain system, consisting of 50 foot sections of $^5/_8$-inch low carbon steel chain (made up of segments from 3 to $3^1/_2$ feet in length) is suspended in the upper section of the kiln. These become coated with slurry and increase heat transfer, facilitating evaporation of water. Back-end (feed-end) temperature is approximately 700° F.

Permanente Developed Unique Process for Utilization of Dust from Kilns

In all portland cement plants, large quantities of finely divided ground solids enter the kiln, and the kiln gases are heavily laden with dust particles extremely small in size (85% minus 325 mesh). In many plants, the dust is recovered, and in some it is returned to the kiln systems.

In early operations, Permanente pugmilled the recovered dust with kiln feed slurry and reintroduced it to the then existing four kilns. This process is generally used in wet process plants. The system had several disadvantages. Permanente's plant was constantly expanding, and the rated capacity of the kilns was constantly being exceeded. Introduction of the dust was an additional load. Secondly, introduction of dust resulted in changes in chemical balance of the mix (the dust containing more lime and less silica than the mix from which it came). Following experimental work over an extended period of time, it was decided to correct the composition of the dust by addition of clay, nodulize the mixture, and reintroduce the resulting nodules to the kiln feed (Figure 3). Addition of the fifth kiln provided an opportunity to develop the process as it is now used (*10*).

Dust is recovered in a vertical electrical precipitation plant containing eight units of five sections each (*27E*). Operating potential is 40,000 to 60,000 volts, and the plant treats 1,000,000 cubic feed of gas (400° F.) per minute. It is normal to rap the collecting units once or twice during each 8-hour shift. The plant operates at 99% collection efficiency. Collected dust drops to hoppers from which it is carried by a screw and airpad conveyor to a dust surge tank of 120 tons capacity. This tank is air agitated through ceramic pads, and a screw conveyor takes the dust to a bucket elevator which discharges into a dust constant head box. Overflow from the head box returns to the dust tank.

Screw conveyors feed the dust from the head box to one of two nodulizing drums. Speed of the conveyors is synchronized with the alternator on the kiln motor drive shaft. Dust is introduced to the nodulizing drum with 3 to 5% clay, introduced as a thin slurry containing 18 to 25% solids. This is prepared from clay blending slurry containing 40 to 50% solids. Clay from the blending tank is pumped to a 7000-gallon storage tank equipped with air agitation. A rubber-lined pump conveys the slurry to a control tank which overflows back to the storage tank. A density controller-recorder maintains flow of a slurry of the predetermined and constant per cent solids to the nodulizing drums.

The nodulizer usually used is an 8 × 17 foot drum equipped with beater-type agitator and scraper and operated at 8.5 revolutions per minute. Formerly the clay slurry was introduced through special alloy nozzles; these were found unnecessary, and it is now fed through a perforated steel pipe. The beater rods, running one third the length of the drum and rotating in the opposite direction provide complete mixing of the dust and clay slurry. Nodules, averaging about 1 inch in diameter, are discharged from the nodulizer to a conveyor system that goes to a point in the kiln below the chain section of kiln No. 5. This kiln is equipped at this point with a nodule scoop feeder consisting of six scoops, each with a 1-foot 9-inch by 1-foot $5^{1}/_{2}$-inch open area (*20E*). The scoops feed the nodules through the walls of the kiln at a point where the temperature is 1200° to 1400° F. At present, the feed to kiln No. 5 consists of approximately 50% nodules (82% solids) and 50% slurry (65% solids) for an over-all average of approximately 73 to 74% solids. Kiln No. 3 is also equipped for dust feed and is used when kiln No. 5 is out of operation.

The system has proved very satisfactory, and several advantages have been experienced (U. S. patent pending). The per cent solids in the feed to the remaining four kilns was boosted from 61 to 65% when dust feed to them was discontinued. Fuel consumption was reduced by $6^{1}/_{2}$%. The increase in clinker capacity from the addition of the fifth kiln was 10 to 11% greater than could have been expected without the nodulizing system. More uniform and smooth burning operation has also been experienced, and the complicated pugmill system, with high maintenance costs, has also been eliminated along with an accompanying horsepower reduction of 40 to 45%.

Under proper operating conditions, clinker emerges from the kiln in the form of rounded, irregular balls ranging in size from $^{1}/_{4}$ to $1^{1}/_{2}$ inches in diameter. They are red hot at kiln discharge (2400° F.). When cooled, they are velvety black or gray black, and many tiny sparkling facets can be observed.

In early plants, the hot clinker dropped or was conveyed directly to the storage pile, where a spray of water was directed upon it. It was sometimes ground when still hot, but it was believed by some that grindability and soundness were improved by storing the clinker for days or even weeks (*6*).

Simple rotary-type coolers, usually installed below the kilns are used in many plants. The integral cooler, essentially an elongation of the kiln, was developed more recently. Inasmuch as the heat content of clinker is high—200,000 B.t.u. per barrel—proper consideration to its recovery and utilization is an important factor in plant design and operation.

At Permanente's plant, the clinker is cooled and heat is recovered in 7 × 44 foot air-quenching coolers of the inclined grate type (*7E*). A cooler is located below and in line with each kiln. The clinker at 2400° F. drops through a chute upon inclined alternately stationary and reciprocating grates, the latter propelling the clinker to the cooler discharge. Air is drawn into the cooler by 77,000 cubic feet per minute fans from below the grates and up through the clinker. Clinker discharges at 100° to 170° F. to a rubber conveyor belt. This portion of the cooler discharge is conveyed to one of two 3-foot cone crushers which reduce the size to minus $1^{1}/_{2}$ inch (*25E*). Finer clinker, which passes through the grates, by-passes the crusher. The combined cooler discharge is conveyed to one of five large concrete clinker storage bins (four of 47,650 cubic feet and one of 52,540 cubic feet). These bins are equipped with feeders, and conveyors below them go to clinker bins in the finish grinding department.

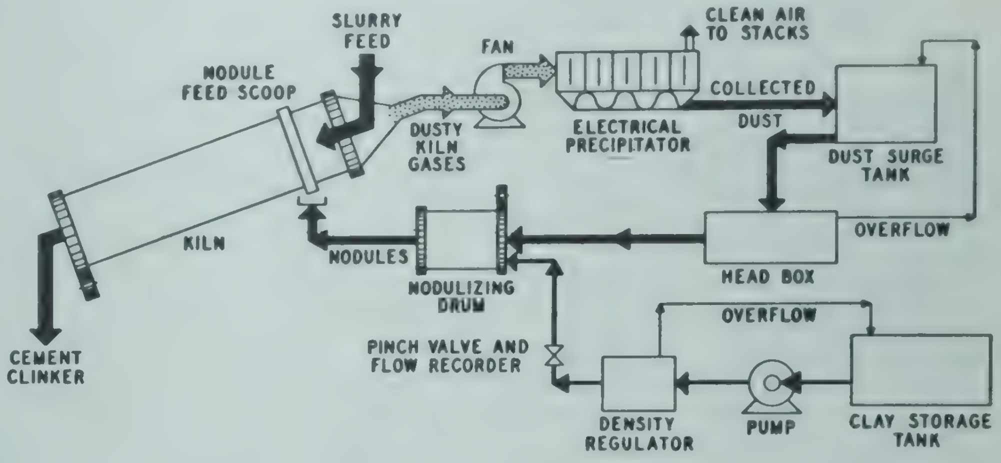


Figure 3. Dust Recovery and Nodulizing System

Dust is recovered from the air discharge from the clinker coolers in mechanical dust collectors with eight 10-inch dust valves (*28E*). Approximately 1.5 tons of dust are removed each hour. From the collectors, it is taken by belt conveyors to the clinker bins in the finish grinding department. The air heated during cooling of the clinker is used as secondary combustion air in the rotary kilns.

Cement Is "Finish" Ground in One of Six Circuits

Finish grinding of the clinker is one of the most important unit processes in cement manufacture. Ball and tube mills in both open and closed circuits and accompanied by various types of air separators are used in the final processing step.

In the finish grind department at Permanente's plant, there are 10 bins that feed the different grinding circuits. These include five for clinker, three for gypsum, and two for admixture of pozzolan and rock used in pozzolan and plastic cement. There are six separate closed grinding circuits (Table VII).

Circuit No. 1 is typical of the six circuits. Clinker and gypsum (3% by weight) are fed to the mill preliminator (a $9^{1}/_{2}$ × 10 foot ball mill). A grinding aid, consisting of triethanolamine and highly purified soluble calcium salts of modified lignin sulfonic acids, is introduced in liquid form at the rate of 1600 cc. per minute (maximum of 0.043% by weight of cement). This

Table VII. Finish Grinding Circuits (Closed)

Circuit	Feed	Preliminators Diameter Ft.	Preliminators Diameter In.	Preliminators Equip. Ref.	Preliminators Length Ft.	Preliminators Length In.	Preliminators Hp.	Tube Mills Diameter Ft.	Tube Mills Diameter In.	Tube Mills Equip. Ref.	Tube Mills Length Ft.	Tube Mills Length In.	Tube Mills Hp.	Separators No.	Separators Diam., Ft.	Equip. Ref.	Cyclones No.	Cyclones Diam., Ft.
1	Clinker gypsum	9	6	(*23E*)	10	0	500	8	0	(*24E*)	40	0	1000	2	16	(*15E*)	1	8
2	Clinker gypsum admixture	9	6	(*1E*)	10	6	500	8	0	(*2E*)	40	0	1000	2	16	(*15E*)	1	8
3	"	9	6	(*16E*)	10	8	500	8	0	(*17E*)	36	0	1000	1	10	(*18E*)	1	9
4	"	9	6	(*16E*)	10	8	500	8	0	(*17E*)	36	0	1000	1	10	(*18E*)	1	9
5	"	9	6	(*16E*)	10	8	500	8	0	(*17E*)	36	0	1000	2	16	(*15E*)	1	8
6	Clinker gypsum	9	0	(*16E*)	10	8	500	8	0	(*17E*)	36	0	1000	2	16	(*15E*)	1	6

Dust is recovered from kiln gases in a vertical electrical precipitation plant containing eight units of five sections each

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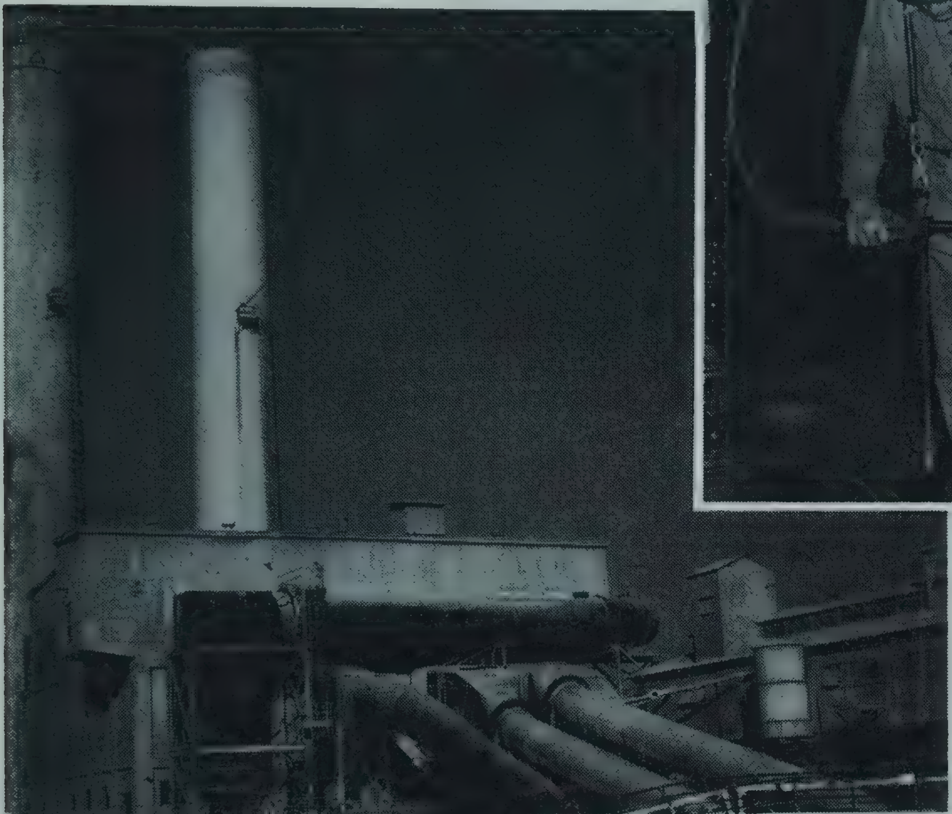

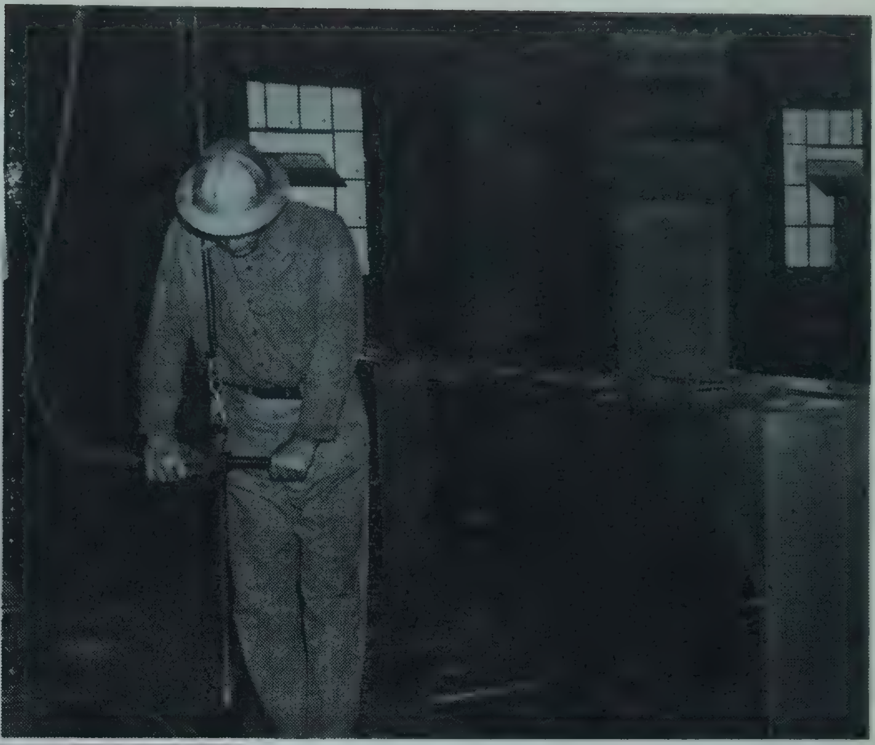

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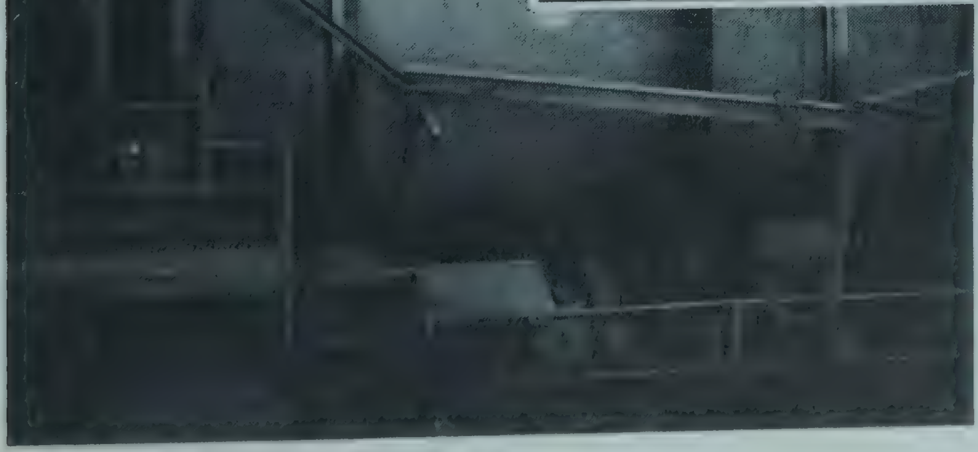
Precipitation house operator raps electrodes once or twice each shift with a jack hammer to remove collected dust so that it can drop to hoppers

▶

Composition of recovered dust is corrected by addition of clay; dust slurry is then converted into nodules in a rotary drum



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Nodules, averaging one inch in diameter, are reintroduced into the fifth of the five kilns keeps the balls free of coating thereby increasing grinding efficiency. Discharge from the preliminator passes directly to the 8 × 40 foot cement tube mill. Discharge from the mill is pumped by a cement pump to a collecting cyclone. In cement pumps, a screw feeds the cement powder into an aeration chamber where air jets admit streams of compressed air which mix with the cement to form a fluid mass (*9E*). The discharge from the cyclone goes to one of two mechanical air separators (*15E*). Coarse particles are recycled to the tube mill. These mills carry a circulating load of 200 to 250%. Fines go by means of a 12-inch airpad conveyor (*8E*) to one of two cement coolers. The air pad conveyor consists of an inclined porous medium (canvass) which supports the cement in the upper portion of an enclosed system. Low pressure air is drawn from below and up through the canvas and cement, reducing the angle of repose to a point (below 4°) where cement is semifluidized and flows. The coolers, designed by Permanente, are chambers containing a bottom constructed of 12 × 12 inch square porous tiles through which air is drawn continuously. Cement enters at 230° to 250° F. and is discharged at 180° to 200° F. From the coolers, the cement goes by means of a 12 inch airpad conveyor to the cement storage silos.

Cement storage includes 27–30 foot diameter by 90 feet high concrete silos, each with a capacity of 15,904 barrels. Star bin space between each four adjoining silos (3780 cubic feet each) is also utilized. Total storage capacity is 490,000 barrels. All silos and star bins are filled through airpad conveyors. From storage silos, cement can be pumped directly to bulk loading cars and trucks or to packing department. In packing department, it can be bulk loaded to trucks or packed by 4-spout baggers into multiwall paper bags holding 94 pounds of cement (*22E*).

Permanente Produces Numerous Kinds of Cement for Specific Applications

Weather conditions in the West range from semitropical heat to subzero cold; arid desert land is separated is some cases by only a few miles from regions of heavy rain. Too, irrigation canals in many areas pass through regions where soil is impregnated with alkaline salts, which are destructive to ordinary concrete. As a result, many types of cement are required to meet all construction requirements.

Permanente manufactures several kinds of cement. Standard portland cement (Type I) constitutes by far the major part of output. Types II (modified portland), III (high early strength), IV (low-heat), and V (sulfate resistant) are produced in smaller proportions for construction projects requiring their particular characteristics. As previously mentioned, Permanente also produces pozzolan cement, which resists sulfate and salt- or fresh-water action better than standard portland cement.

The company also makes a modified high early strength cement, ground finer than standard portland cement to produce a plastic concrete which sets rapidly. This product is used in making cement pipes and makes possible the daily production of hundreds of pipes from a single mold machine. A cement mortar, composed of portland cement with additives and plasticizers, is used to make a waterproof joint between bricks. Exterior cement stucco is a mixture of a special cement (composed of standard portland interground with plasticizing agents) with sand and water. Four types of oil well cements, which have properties for widely spread demands of the oil industry, are produced through careful control of their chemical composition.

Factors of Cost in Cement-Making Vary Widely

Plant location, proximity to raw materials, quality of raw materials, labor supply, and utility rates all materially affect the cost of production of portland cement. However, in contrast to many industries, fuel is the single most expensive cost component in a barrel of cement. Over the country, this constitutes from one quarter to one third of the cost of manufacture. Raw materials, on the other hand, represent a comparatively smaller part of the cost, ranging from a very minor portion to a maximum of one half the over-all cost.

The portland cement industry is highly mechanized. As outlined in this report, there are many extremely large pieces of machinery and equipment. Maintenance, therefore, is a major item of operating costs. Labor costs vary widely—production per man-hour ranges from 2$^1/_2$ to 8 barrels of cement. Power consumption is from 18 to 25 kw.-hr. per barrel. Though processing water is extensively re-used, consumption is still high. (Permanente discharges approximately 400 gallons per minute to atmosphere with kiln exit gases.)

Other important factors are grinding balls in the ball-and-tube mills, mill liners, and kiln brick. When bagged, the cost of bags is a significant factor. Additional charge per barrel (four sacks) is from 30 to 40 cents as compared with bulk shipment. Even this does not in general represent the total cost of the bags themselves plus packing expenses. In the past 5 to 6 years at Permanente, the trend has been heavily in the direction of bulk shipment. There has also been a marked increase in bulk shipping by truck in comparison with rail shipment. Improved, lightweight bulk trucks have been introduced in the past year or two. Permanente has added a fleet of these carriers to its formerly much smaller number of bulk trucks.

Four-Spout Packing Machines Fill 28 Sacks (94 Pounds Each) per Minute

Portland Cement Industry Looks to Continued Growth

The growth of Permanente's cement plant from an original two kilns to five in only 13 years points up in a dramatic way the future of the western portland cement industry. Some of the expansion was simply the result of location in the fast growing West and increased requirements for building materials during the period of World War II and since. Permanente's unique transportation system for low cost bulk cement, which encompasses a distribution range of more than 2000 miles versus the 200 to 300 miles for the average cement company, has contributed to the company's growth.

But, on a national scale, the phenomenal growth of the industry and the optimistic outlook for its future are results of a planned and energetic program directed toward the development of new uses of portland cement and improved techniques of application. It has been said that more progress was made in developments affecting portland cement in the first 2 years of World War II construction than any previous 10-year period (*16*). Many war-time developments—which expedited construction and saved labor, time, and money—are being applied to advantage in civilian projects.

A few of the technical advances bear mentioning. Much work has been done relating to fire resistance, insulation, and acoustics. As a result, concrete walls can now be insulated for almost any range of temperature changes; concrete mixtures can be designed to have either low or high conductivity properties; soundproofness and desired acoustical characteristics can be incorporated.

Techniques have been developed which have increased the water tightness of concrete. At present, any good contractor can make concrete mixtures with any degree of water tightness; at the same time, mixtures range from densities as low as 30 pounds per cubic foot to 250 pounds per cubic foot. These mixtures can be made in an almost unlimited number of colors and color combinations.

In construction, there have been many advances in prefabrication of concrete buildings, which have and will further increase markets for portland cement in house construction. There has also been marked improvement in concrete floor and roof design. Prestressed concrete pipe, tanks, and bridges have received much study and are becoming commonplace.

While there is some shifting in the order of portland cement uses (Table II), all continue to increase, and the future growth of the industry seems ensured.

Acknowledgment

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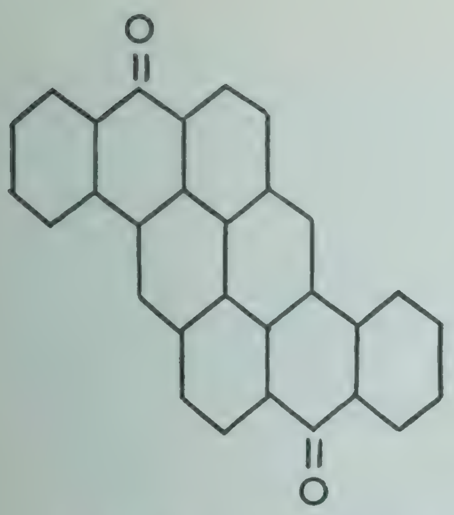
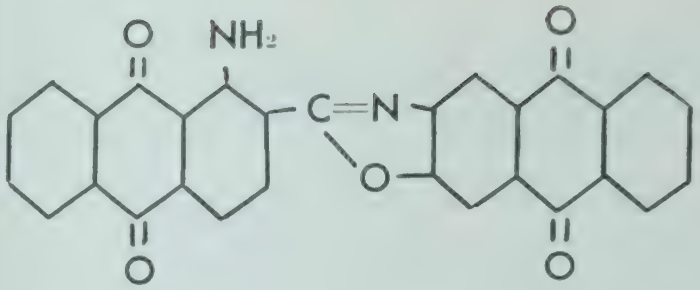
(29E) Wooldridge Manufacturing Co., Sunnyvale, Calif., Model 14 Terra Cobras.

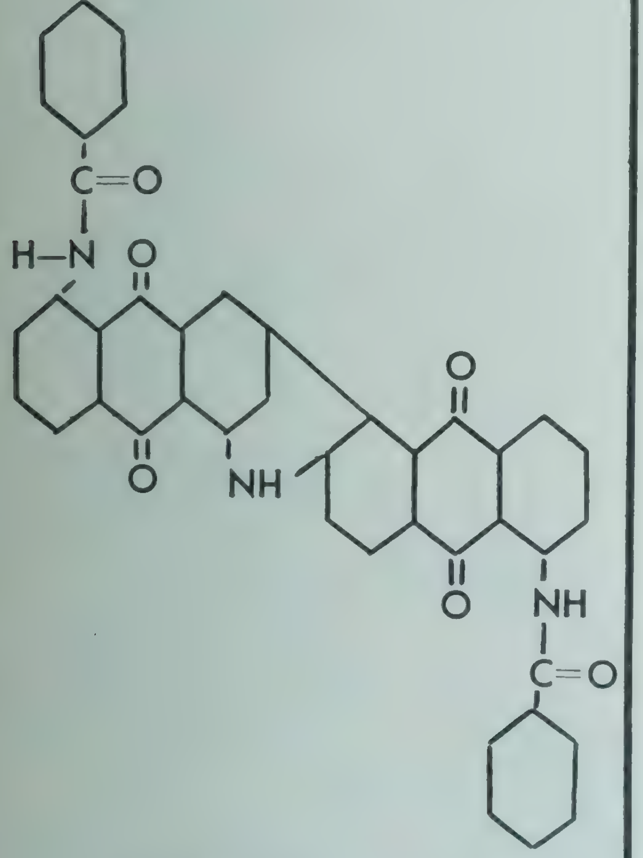
This article appeared in Vol. **46**, *page 830* (*May, 1954*).



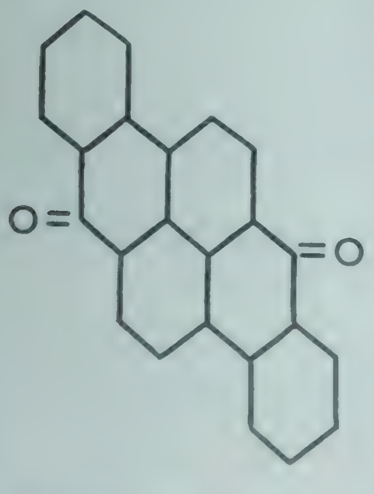
GOLDEN ORANGE G



RED FBB



GOLDEN ORANGE 3G



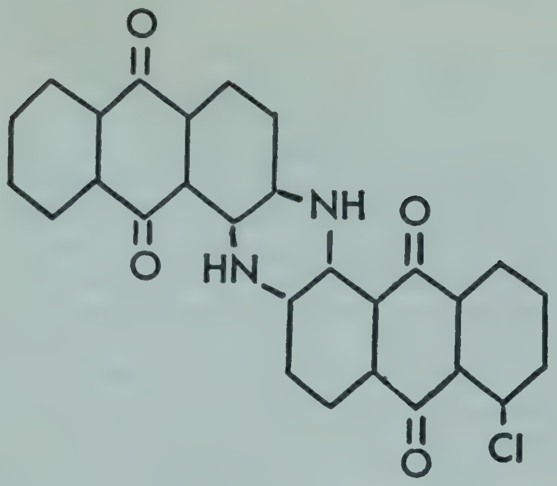
GOLDEN YELLOW GK

Anthraquinone

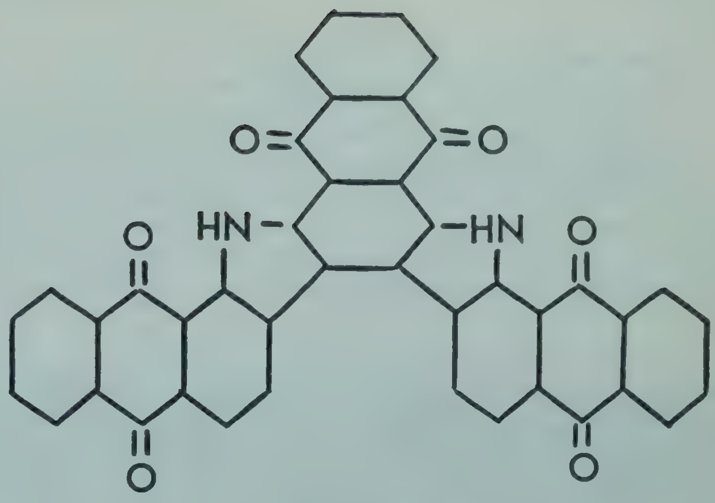
SINCE WORLD WAR II, the most outstanding increase in synthetic dyestuff production in the United States has been in the class of vat dyes. Output averaged 30.9% of total U. S. synthetic dyestuff production in the years 1946 to 1950. It increased to 36.2% in 1951 and to 39.4% in 1952. In 1952, 24.8% of all synthetic dyes produced in this country were anthraquinone vat dyes (*4*). These dyes, in the commercial range, are outstanding for fastness to light, washing, and many other agencies. They are second only to azo dyes in quantity of production but probably surpass the azos in money value.

Production of anthraquinone vat dyes was relatively high in 1951 but fell off considerably the following year (Table I). This was largely due to the demand for anthraquinone vats for coloring military uniforms in 1951 and the practical disappearance of that business in 1952. Khaki 2G, Olive T, Olive 2B, Brown BG, Olive 2R, and Brown BR were most seriously affected by this demand fluctuation.

René Bohn, in 1901, synthesized the first members of the anthraquinone vat family, indanthrene (now called indanthrone) and flavanthrene (*2, 5*). The same year, both dyes were placed on the market by the Badische Anilin- und Soda-Fabrik. These were the first dyes possessing not only a carbon skeleton differing from indigo but also an entirely different chromophoric residue (*2*). An adequate number of dyes fast to wool and silk were



BLUE GCD



BROWN BR

Vat Dyes

KEVIN J. BRADLEY, *Assistant Editor*

in collaboration with

PHILLIP KRONOWITT

Ciba States Limited, Toms River, N. J.

available, but until the advent of the anthraquinone vats, there were no reliable, fast dyes for cotton. Indanthrone is seldom used today because of its sensitivity to bleaching agents.

Vat dyestuffs are so named because of their ability to form a soluble alkali salt or vat from the insoluble dye (*5*). This is usually accomplished by an alkaline reducing agent, and the affinity of the colorless leuco salt for textile fibers, especially cellulosic fibers, is characteristic of the group. The insoluble dye is regenerated on the fiber by oxidation, usually with atmospheric oxygen. Practically all anthraquinone vat dyes contain a pair of carbonyl groups, either as a 1,4-quinone or as part of a complex quinone system in a polycyclic aromatic compound. Most anthraquinone derivatives contain two or more anthraquinone ring systems.

Prior to World War I, anthraquinone vat dyes were made almost exclusively in Germany. Since 1907, they have been manufactured at Basle, Switzerland, by CIBA (Society of the Chemical Industry in Basle). The war-stimulated growth of the chemical industry resulted in the manufacture of vat dyes in Great Britain, the United States, France, Italy, and Japan, in the World War I years and in the twenties. However, Germany remained the leader, a position strengthened by the amalgamation of the German dyemakers into the IG in 1924.

Market Expansion Led CIBA to Build in the United States

Expansion of the American market for anthraquinone vat dyestuffs in the period after World War II encouraged CIBA to look for a plant site on this continent. Land was purchased in June 1949 at Toms River, N. J. Space for expansion and nearness to raw materials and market were determining factors in the choice. Of the 1250 acres purchased, about 35 acres have been cleared of trees. Although the location is near the North Jersey heavy manufacturing areas, cranberries, blueberries, poultry, and vacationists are the main income producers of the immediate neighborhood. Water is available from the river, but it has been found that the ground water in the area is of such superior quality that a minimum of treatment is required for its use as process water. Toms River, served by two railroads and excellent hard-surfaced highways, is 53 miles from Philadelphia and 70 miles from New York. It is easily accessible to major markets and principal distribution centers along the Atlantic coast.

The plant, built at a cost of $18,000,000, is designed for a normal production capacity of 4,000,000 pounds of paste dyestuffs a year. About 35 colors can be produced, depending on market requirements. Besides those listed in Table III, several new dyes, developed recently by CIBA, will be made. The whole list includes dyes ranging from yellows to blacks, but almost all have a common denominator in anthraquinone. Economics at present favor purchase of this material from large manufacturers; however, CIBA could make its own anthraquinone at Toms River from phthalic anhydride and benzene.

Table I. Production and Sales of Anthraquinone Vat Dyes (4)

	Production, Thous Lb.	Sales		Unit Value per Lb.
		Thous. pounds	Thous. dollars	
	All Anthraquinone Dyes			
1952	43,931	43,587	63,117	1.46
1951	51,579	41,484	60,023	1.44
1950	40,742	35,979	53,031	1.47
1949	29,310	28,298	40,513	1.41
1948	31,673	27,961	38,335	1.37
1947	27,192	25,753	32,505	1.26
	Brown BR			
1952	310	336	696	2.07
1951	688	440	986	2.24
1950	589	457	1,014	2.22
1949	514	450	970	2.16
1948	528	416	768	1.85

Manufacturing Processes Requiring Use of Flammable Solvents Carried Out in Separate Building

The manufacturing part of the Toms River plant is composed of three buildings: two production units and, located between them and connected to each by two-story bridges, the five-story standardization building. Although the standardization building is higher than its two companions, it contains less floor space. Each of the production buildings contain about 1,500,000 cubic feet, while the standardization building contains 950,000 cubic feet. The production buildings are very similar to each other; they are three stories in height and contain much the same equipment. One is designed for processes that can be carried out in aqueous or other nonflammable reaction media. Its twin is intended for those processes that involve the use of organic solvents, and it is equipped with the latest devices to reduce hazard from flammable and toxic solvents.

Battery of Glass-Lined and Cast-Iron Reaction Vessels

Stairways in both buildings are of the fire tower type, constructed outside the building proper and independent of it. The solvent building fire towers have an open balcony on each floor. All windows in the solvent building are equipped with explosion latches so that an explosion will blow them open easily and dissipate its force. All electrical apparatus in this building is explosionproof. Every reaction vessel in both process buildings is connected to a plant-wide vent system leading to washer type fume exhausts on the roofs. Hinged vent ducts can be swung directly onto the vessel outlets and hitched with quick-closing connections. All ventilation ducts are of lead sheet or plastic. Both process buildings are of central well construction, facilitating the shifting of equipment and making ventilation easier.

Production Buildings Equipped with Motor-Driven Roof Ventilators

In case of emergencies such as broken fume lines, motor-driven ventilators mounted on the roofs of the production buildings can change the air in an entire building in 5 minutes. Portable explosimeters and electronic vapor detectors are used to indicate any potential hazard. Gas masks, emergency showers, eye rinsers, and other conventional safety equipment are readily available.

There is one maintenance man for every production worker in the plant. Volunteers from the 325-man working force comprise a trained fire brigade to run the high pressure fog-type fire pumper. Periodic fire drills are held. The plant-wide fire alarm system records all alarms on tape in the pump house.

Maintenance workers entering a vessel wear a safety harness and are under continuous supervision by a person outside the vessel. The equipment is cleaned and ventilated before entrance is permitted. Fresh air is supplied continuously to the interior of the vessel. Grinding and mixing of dry powders is done in a closed circuit. Powder loading, unloading, filling, and weighing are carried out under hoods with exhausters and dust-collecting equipment.

A control laboratory is on the top floor of the central finishing building. Reactions are sampled in the process buildings, and samples are checked in this laboratory. Use tests on the finished dyes are also carried out here. Cloth swatches or lengths of yarn are dyed on a laboratory scale, and the dyed material is checked for shade, strength, fastness to light, washing, and other agents and ease of application. Particle size is checked here by sieve tests and microscopic examination, and various filtration tests are made to determine insoluble residue.

Liquid raw materials are stored in a tank farm consisting of eight 12,000-gallon tanks, located adjacent to the railhead. Two of the tanks contain sulfuric acid and two more are for oleum. Caustic, aqueous ammonia, hydrochloric acid, and benzene are also stored in the farm. Pumps (*8E*) are mounted directly on these storage tanks. Liquid chemicals are pumped from the tank farm to the process buildings through overhead pipelines, which include mild steel, rubber-lined, and lead-lined ducts. Most organic solvents are stored in an underground tank farm adjacent to the solvent building.

Processes in both the production buildings begin on the second floor. Liquids pumped from the tank farm are held in storage tanks mounted in a tower section. These storage tanks can hold 2500 gallons, from 2 day's to a week's supply. Measuring tanks (*19E*) are located on a platform between the second and third floors directly behind the reaction kettles. These tanks are equipped with teller gages for volume measurement and are fed from the storage tanks by gravity flow. Both storage and measuring tanks are made in different materials for different liquids. Those designed to hold hydrochloric acid are rubber-lined; for caustic or concentrated sulfuric acid they are mild steel; stainless steel is used for aqueous ammonia and lead linings for dilute sulfuric acid.

Table II. Reaction Vessels

No. Vessels	Description	Size, Gallons
Nonjacketed		
3	Mild steel	4000 to 5000
1	Cast iron	4000
30	Mild steel, acidproof, brick-lined	2500 to 5000
11	Mild steel, rubber-lined	2500 to 4000
Jacketed		
20	Cast iron	250 to 1500
2	Mild steel, lead-lined	1000
4	Stainless steel	750
1	Mild steel, nickelclad	750
19	Mild steel, enameled	250 to 1500

There are about 100 reaction kettles varying in capacity from 250 to 5000 gallons (Table II) in the two process buildings. They are set into the second floors, which serve as working platforms. Kettles are grouped in batteries designed for a given type of reaction (Figure 1). Sulfonations, halogenations, aminations, reductions, condensations, oxidations, saponifications, and nitrations are carried out in these kettles. Many are jacketed for heating or cooling by hot or cold water, brine, or steam; others have provision for heating and cooling by means of coils or open steam. Coils and open steam outlets are of corrosion-resistant alloy *(7E)*, lead, or steel. All reaction vessels are equipped with vertical motor-driven agitators. Some have motor ammeters to indicate overloading and consequent overheating. Stirrers are mild steel or cast-iron, lead, glass, or rubber-covered steel, or corrosion-resistant alloy. Some of the vessels have bottom outlet valves; others utilize blow legs (lead, corrosion-resistant alloy, enameled or rubber-covered steel). Some of the blow legs (outlet pipes starting at the bottom of the tank and going up the side and out) are permanently attached; others can be raised above the liquid level or taken completely out of the vessel. There are four jacketed, high pressure autoclaves *(1E)* with volumes ranging from 500 to 2500 gallons, all in the acid building. These vessels are constructed of mild steel, clad with stainless steel. They are heated by means of a Dowtherm system *(5E)* with the heating unit *(24E)* located outside the process building. Several reaction kettles in the solvent building are heated by Dowtherm. In this case the heating unit is located 50 feet from the building wall to reduce fire hazard.

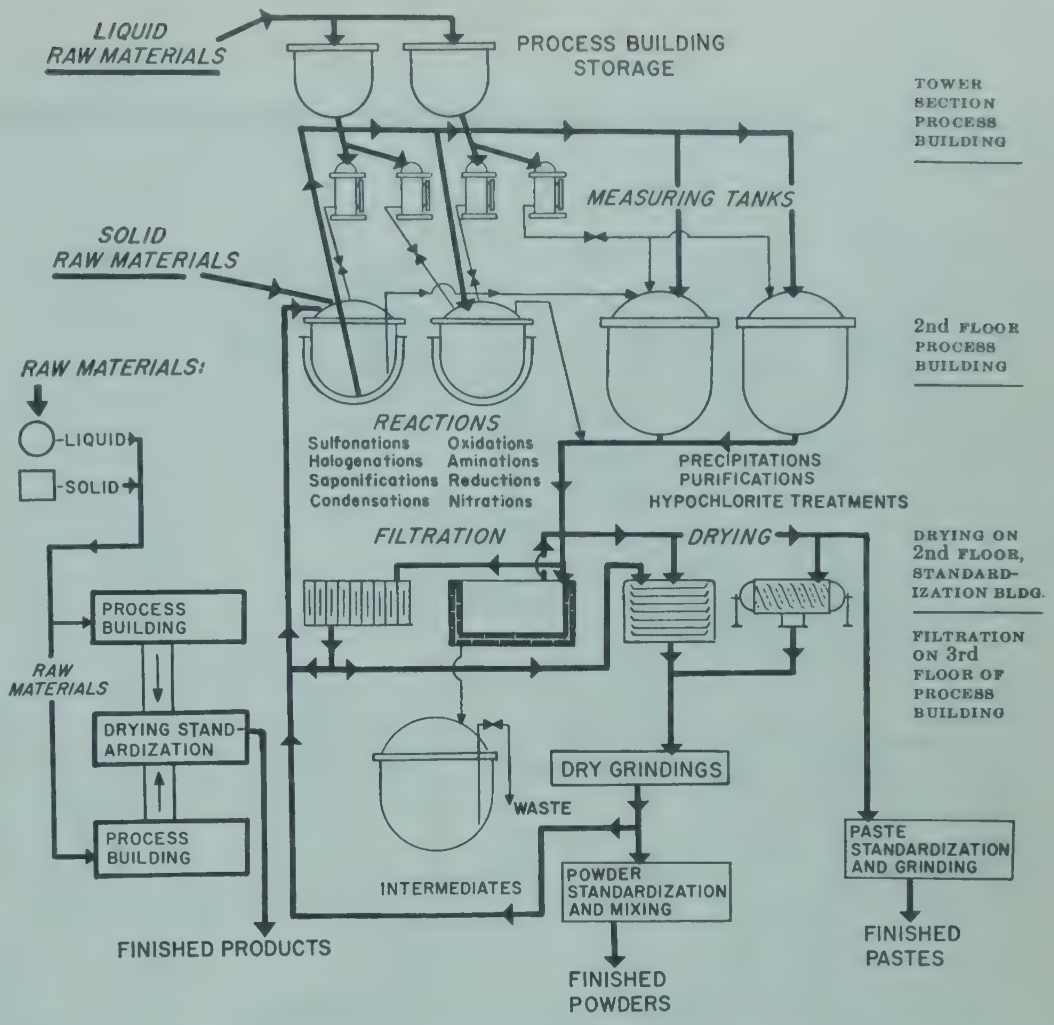

LIQUID RAW MATERIALS
PROCESS BUILDING STORAGE
TOWER SECTION PROCESS BUILDING
MEASURING TANKS
SOLID RAW MATERIALS
2nd FLOOR PROCESS BUILDING
RAW MATERIALS:
-LIQUID
-SOLID
REACTIONS
Sulfonations
Oxidations
Halogenations
Aminations
Saponifications
Reductions
Condensations
Nitrations
PRECIPITATIONS
PURIFICATIONS
HYPOCHLORITE TREATMENTS
FILTRATION
DRYING
DRYING ON 2nd FLOOR, STANDARDIZATION BLDG.
FILTRATION ON 3rd FLOOR OF PROCESS BUILDING
PROCESS BUILDING
RAW MATERIALS
DRYING STANDARDIZATION
PROCESS BUILDING
DRY GRINDINGS
WASTE
INTERMEDIATES
POWDER STANDARDIZATION AND MIXING
PASTE STANDARDIZATION AND GRINDING
FINISHED PRODUCTS
FINISHED POWDERS
FINISHED PASTES

Figure 1. Multipurpose Equipment Available for Production of Anthraquinone Vat Dyes, Toms River, N. J., Plant of Ciba States Limited

Piping System Connects Groups of Apparatus Designed for Processing Similar Reactants

Permanent piping systems lead to group switching stations where flexible connections can send material from any battery of reaction kettles to any group of filtering units or to other tanks for further treatment. For example, the group of enameled kettles is connected to the switching station by porcelain piping and similarly from the station to the acidproof brick–lined filters. Flexible connections are of rubber or of lead or rubber-lined mild steel. Filtration is accomplished in filter presses, suction filters, or pressure filters, generally on the third floor.

Filter presses *(14E)* are open delivery washing type plate-and-frame units with cotton, wool, Dynel, or Vinyon N filter cloth. The process buildings contain 20 cast-iron presses and 19 of wood. They have 30 to 40 chambers apiece; frame size is 42 inches square by 2 inches deep. Four of the filter presses in the solvent building are enclosed under sectional aluminum hoods running on rails. Fumes from these presses are exhausted through a separate vent system.

The suction filters are steel boxes *(23E)* lined with acidproof brick *(17E)*. A porous stone filter bottom makes them useful in handling acid filtrates. Filter area ranges from 80 to 150 square feet for the 17 units in the plant. Suction is obtained from motor-driven piston-type vacuum pumps *(16E)* located in the process buildings.

Pressure filters *(3)* are cylindrical tanks *(20E)* containing 70 square feet of filter area. They are equipped with flat stirrers which parallel the filter bed. One pressure filter is acidproof brick–lined and equipped with a porous stone filter; another has a wool filter cloth and the third, cotton. The porous stone does the best filtration job but is subject to clogging when filtrate crystallizes in the stone. The stirrers can be raised or lowered and are used to keep the filter cake from cracking and also to push the pulp out through three ports in the side of the filter.

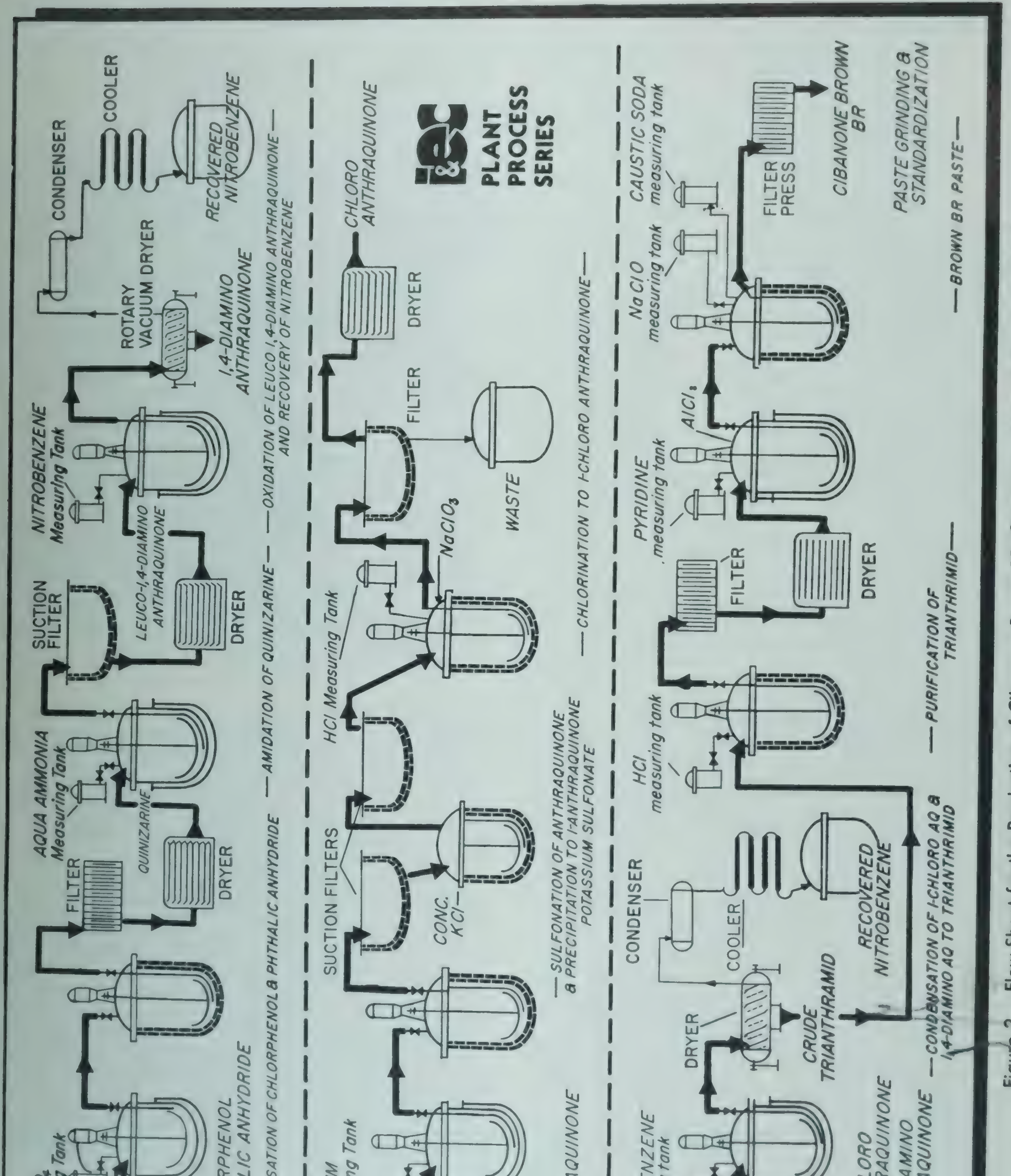
Pressure can be exerted through the reaction vessels to the filters by either compressed air or inert gas, both at 45 pounds per square inch. The inert gas, produced in the power plant building by controlled combustion of propane *(13E)* is used whenever use of compressed air would result in a fire hazard.

Filter cake is transported in carts called "cake cars," which are hitched together into trains and drawn by small tractors. They are run from one operational area to another via the bridges connecting the third floor of each production building with the drying and paste-charging floor of the standardization building. Few of the dyestuffs are dried; most are standardized as to shade, concentration, and physical form and sold as pastes.

Intermediates and some dyes are dried on the fourth floor of the standardization building. Both oven-type air dryers *(11E)* and vacuum chamber dryers *(4E)* are available, and where drying requirements are not too stringent, they are used interchangeably as production needs permit. Both types of dryers utilize stainless steel trays for the filter cake. In the vacuum chamber dryers, the trays are placed on heated shelves. Trays can be stacked on trucks and wheeled into the air dryers.

Versatile Equipment Can Be Used as Dryers, Stills, or Reactors

Rather unique pieces of equipment at the Toms River plant are the Venuleths *(3)* which can be used as dryers for aqueous slurries, agitated stills for recovery of solvents by direct atmospheric distillation, agitated steam stills, or reaction vessels



H₂SO₄ Measuring Tank
CHLORPHENOL
PHTHALIC ANHYDRIDE
FILTER
AQUA AMMONIA Measuring Tank
QUINIZARINE
DRYER
SUCTION FILTER
LEUCO-1,4-DIAMINO ANTHRAQUINONE
DRYER
NITROBENZENE Measuring Tank
LEUCO-1,4-DIAMINO ANTHRAQUINONE
ROTARY VACUUM DRYER
1,4-DIAMINO ANTHRAQUINONE
CONDENSER
COOLER
RECOVERED NITROBENZENE
—CONDENSATION OF CHLORPHENOL & PHTHALIC ANHYDRIDE—
—AMIDATION OF QUINIZARINE—
—OXIDATION OF LEUCO 1,4-DIAMINO ANTHRAQUINONE— AND RECOVERY OF NITROBENZENE
OLEUM Measuring Tank
ANTHRAQUINONE
SUCTION FILTERS
CONC. KCl
HCl Measuring Tank
NaClO₃
FILTER
WASTE
DRYER
CHLORO ANTHRAQUINONE
I&EC PLANT PROCESS SERIES
—SULFONATION OF ANTHRAQUINONE & PRECIPITATION TO 1-ANTHRAQUINONE POTASSIUM SULFONATE
—CHLORINATION TO 1-CHLORO ANTHRAQUINONE—
NITROBENZENE measuring tank
1-CHLORO ANTHRAQUINONE
1,4-DIAMINO ANTHRAQUINONE
DRYER
CONDENSER
COOLER
CRUDE TRIANTHRAMID
RECOVERED NITROBENZENE
HCl measuring tank
FILTER
DRYER
PYRIDINE measuring tank
AlCl₃
NaClO measuring tank
CAUSTIC SODA measuring tank
FILTER PRESS
CIBANONE BROWN BR
—CONDENSATION OF 1-CHLORO AQ & 1,4-DIAMINO AQ TO TRIANTHRIMID
—PURIFICATION OF TRIANTHRIMID—
—BROWN BR PASTE—
PASTE GRINDING & STANDARDIZATION

Figure 2. Flow Sheet for the Production of Cibanone Brown BR, Ciba States Limited, Toms River, N. J.

Material Requirements for 100 Pounds of Brown BR and Intermediates

	Pounds
Quinizarin	
Phthalic anhydride	65
p-Chlorophenol	57
Concd. sulfuric acid	435
1,4-Diaminoanthraquinone	
Quinizarin	120
Sodium hydrosulfite	130
Aqua ammonia	1100
1-Anthraquinone potassium sulfonate	
Anthraquinone	89
Oleum 20	218
Potassium chloride	53
1-Chloroanthraquinone	
1-Anthraquinone potassium sulfonate	140
Hydrochloric acid	180
Sodium chlorate	50
Trianthrimid	
1-Chloroanthraquinone	96
1,4-Diaminoanthraquinone	45
Soda ash	22
Sodium acetate	22
Brown Br[a] (100%)	
Trianthrimid	92
Pyridine	465
Aluminum chloride	100
Caustic soda	225
Sodium hypochlorite (13%)	184

[a] Includes carbazolation.

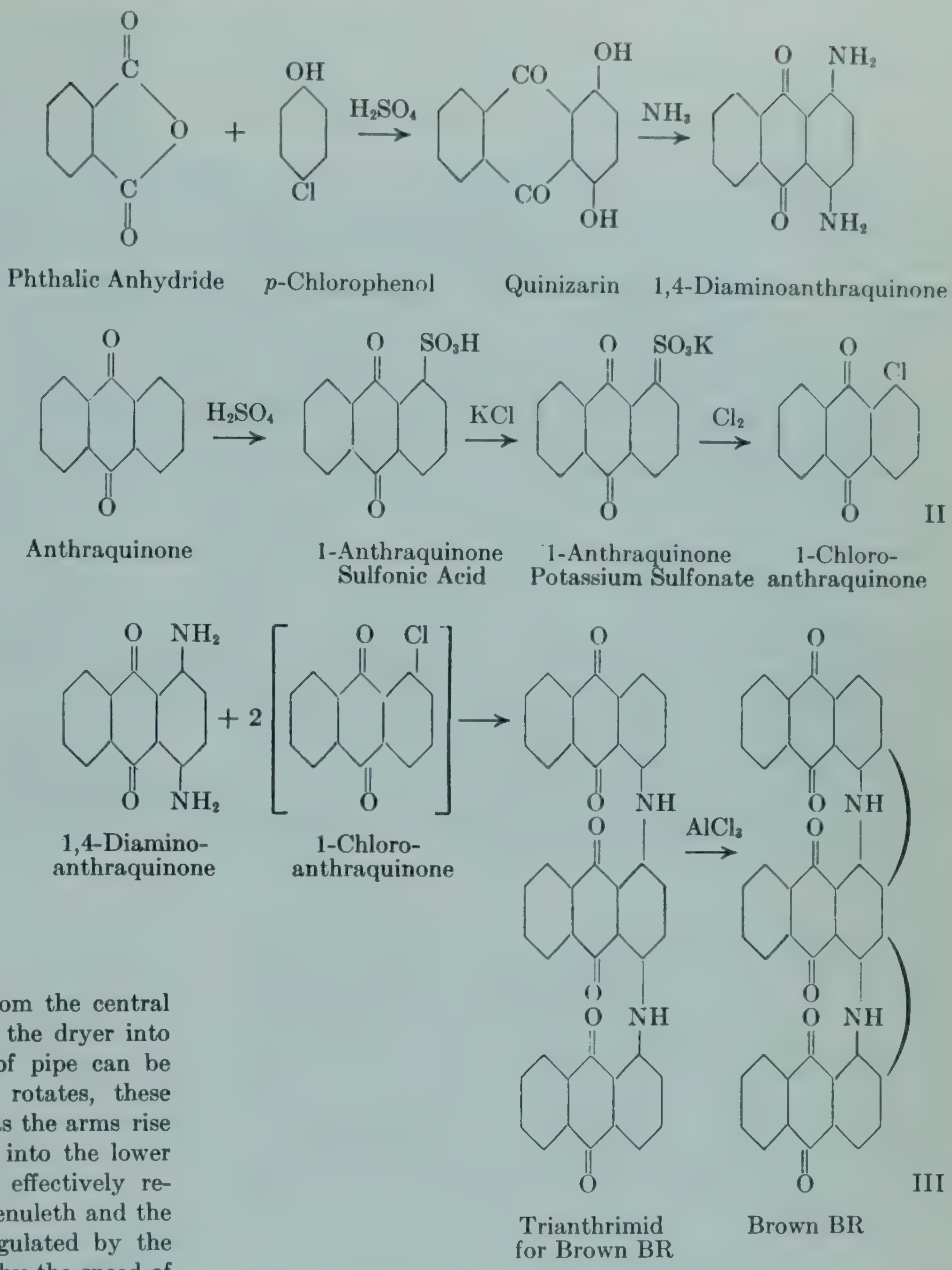


Figure 3. Chemical Structure of Brown BR and Intermediates

(*21E*). They resemble standard horizontal, agitated, jacketed vacuum dryers, and their main use in this plant is as rotary vacuum dryers attached to condensers for the recovery of solvents.

Agitator blades are heavy arms extending from the central horizontal shaft in rows, dividing the interior of the dryer into four quadrants. Pieces of shafting or lengths of pipe can be placed in each quadrant. When the agitator rotates, these weights fall along the arms to the central shaft as the arms rise and then descend along the arms as they move into the lower quadrants. This scraping and grinding action effectively removes lumps and crusts from the walls of the Venuleth and the agitator arms. The grinding action can be regulated by the size weight, and type of the pipe or shafting and by the speed of rotation of the agitator. A reversing motor makes it possible to change the direction of the agitator. This may be done at short intervals to ensure thorough mixing. The rough grinding results in ready discharge of the product from the Venuleth. House vacuum of 28 to 29 inches is augmented by a steam jet vacuum pump (*3E*) on each unit. Operating vacuum may reach 10 to 15 mm. of absolute pressure.

Anthranquinone Derivatives May Be Purified by Sublimation

Another piece of specialized apparatus is a vacuum sublimer (*2E*). The sublimer is used for the purification of several intermediates, such as benzanthrone and the aminoanthraquinones. Anthraquinone derivatives will usually sublime readily. The sublimation apparatus consists of two horizontal cylindrical shells, flush at the top (*3*). The smaller cylinder is the subliming chamber and is closed at one end by a headplate carrying horizontal rows of return bend electrical resistance heaters. These heaters extend the length of the subliming chamber. The metal trays containing the material to be sublimed are placed on a tray truck carried between the heating elements on an overhead trolley.

The larger cylinder is the condensing chamber. It is closed at one end by a solid cylindrical flanged door, suspended from an I-beam by a movable trolley carriage. The door can be rolled into place and makes a vacuum-tight connection with the sublimer. The condensation chamber is cooled by means of a water spray over the outside wall. The heating cycle required for the complete sublimation of an intermediate is known, and the process is automatically controlled by thermocouples.

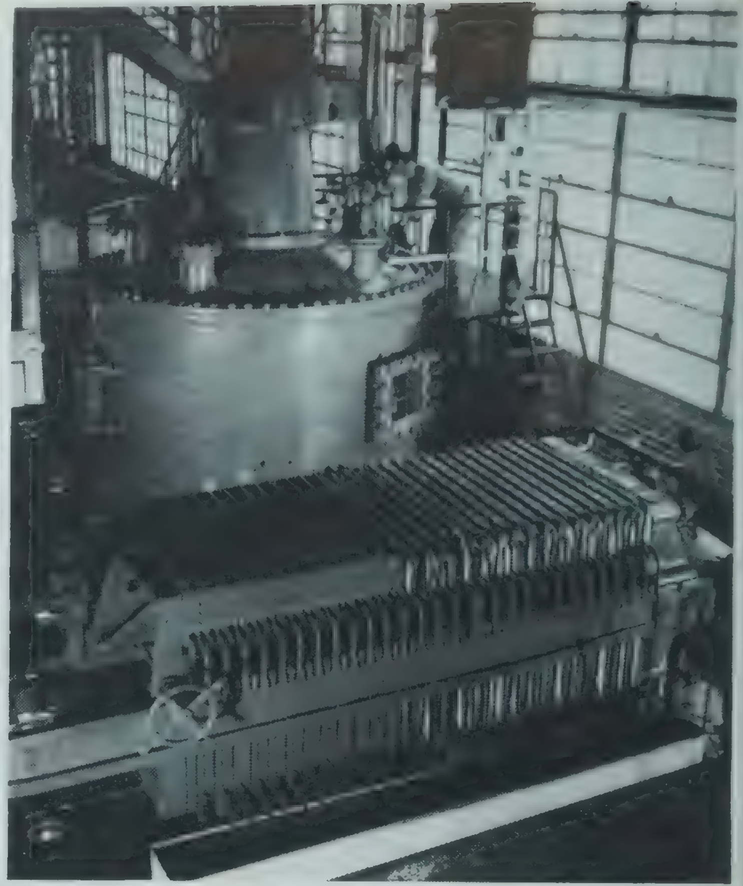
In actual operation, the dry product to be sublimed is loaded in the trays between the rows of heating rods in the sublimation chamber. The equipment is evacuated to about 29 inches of vacuum by a combination of mechanical vacuum pumps and a three-stage steam-jet vacuum pump (*3E*). Vacuums as low as 1 to 2 mm. may be obtained. When evacuation is complete, the current is turned on in the resistance heaters. Sublimation temperatures range from 200° to 350° C., depending on the heat sensitivity of the product. When the necessary temperature is reached, the intermediate sublimes over and condenses in the relatively cool outer chamber. A filter over the vapor outlet prevents loss of the sublimed product.

When the sublimation is judged to be complete, current is switched off in the heaters and the subliming chamber, which is jacketed, is cooled. Slow heat loss is produced by cooling first with steam, then with hot water, and finally with cold water. The purified product is unloaded manually.

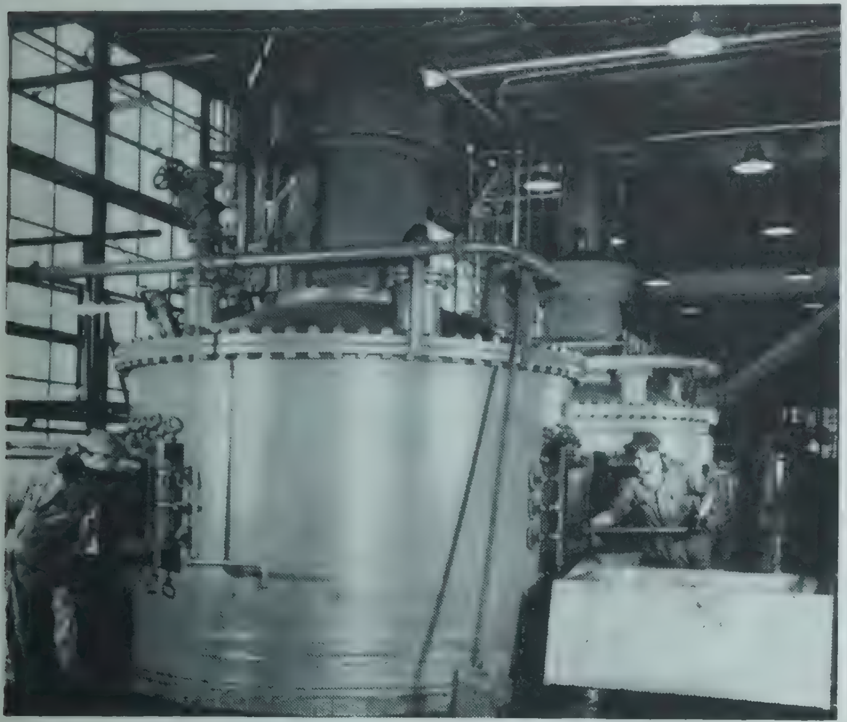
Steam Plant Burns Oil or Pulverized Coal

Two high pressure boilers, oil- or pulverized coal-fired, are housed in the steam power plant. They are operated from an

Pressure Filter Behind Cast-Iron Plate-and-Frame Filter Press Is Used for Filtrations Involving Organic Solvents ▶



▼ Filter Cake Is Unloaded Manually from Pressure Filters



automatic combustion control panel which handles the entire steam operation from the delivery of coal or oil to the railroad tracks outside the powerhouse until steam is sent through the mains to the various buildings. An increase in steam demand, indicated by a corresponding drop in steam pressure, causes instruments controlling the fuel, draft, and feed water to increase these automatically and maintain uniform steam pressure. The furnaces can be switched to or from oil or powdered coal firing automatically, with no change-over delays. The furnace walls are water cooled, since they are surrounded by the water tubes of the boilers.

Coal is received in hopper cars and fed to a crusher and a roundabout conveyor, which feeds the powdered fuel at 50 tons per hour into three reinforced tile coal silos of 1000 tons storage capacity. The same conveyor transports the coal from the silos to bunkers in the boiler room. Ashes are unloaded pneumatically by steam jet exhausters and discharged into a 60-ton reinforced tile silo. Ash removal trucks are fed by a dustless unloading conveyor.

The plant produces 100,000 pounds of steam per hour, at a pressure of 150 pounds gage and with a 50° superheat. Provision has been made for future expansion, and when the plant is equipped with extraction turbines it will operate at 500 pounds and 150° superheat.

Electricity is purchased at 33,000 volts. It is stepped down to 2400 volts at delivery and distributed to the manufacturing buildings. Substations near the individual buildings transform the power to 440 volts for use.

Deep Wells Are the Chief Source of Process Water

When the plant site was picked, the Toms River was considered to be the future source of water for the plant. However, during construction, wells were dug that showed the ground water to be of excellent quality and very abundant. The consulting analytical laboratory which tested samples of this well water even questioned several samples, thinking that someone had inadvertently substituted distilled water. Consequently, about 2,000,000 gallons of water per working day are now supplied by five deep wells with a combined capacity of 2250 gallons per minute. The expensive purifying equipment that would have been necessary for use of water from the Toms River has never been built.

An elevated water tank of 300,000 gallons capacity is fed by the wells. It provides a 160-foot constant head. Two standpipes, one for the fire hydrant and sprinkler system and another for process water, provide 300,000 gallons for fire protection and 150,000 gallons reservoir for plant water.

Plant Effluent Is Neutralized, Sedimented, Oxidized, and Chlorinated

Since the CIBA plant is located in an area where two of the most important industries are fishing and vacationists, elimination of any interference with these activities is basic to good community relations. The plant effluent varies from 1.0 to 11.0 in pH and often contains a large amount of highly colored solids. Its probable effect on aquatic life, if discharged directly into the river, would be harmful.

Process wastes are collected in a 2,500,000-gallon equalization basin lined with asphalt (*1*). The raw plant effluent is discharged into a distribution trough which feeds the basin evenly through a series of tile lines. A similar trough at the other end of the basin collects the equalized effluent and feeds the neutralization basin through a flow-regulating gate. The equalization basin has a retention capacity of 1 to 1.5 day's flow. Plant sanitary sewage is treated in an anaerobic digestion unit, and most of the clear effluent is added to the equalization basin. The combined effluent, ranging from pH 2.0 to 3.6, is neutralized with lime solution in a four-compartment, acidproof brick-lined neutralization basin. Four motor-driven stirrers mix effluent with lime, which is added at a controlled rate. This step is completely automatic as to rate of addition of the lime solution and the final pH. An automatic pH recorder-controller actuates the lime solution pumps and motor-operated valves.

A conveyor system carries the lime from hopper cars on the railroad siding to the 50-ton steel storage hopper. The lime is slaked and the solution stored in a concrete tank. It is fed from

Table III. Cibanone Vat Dyes Produced at Toms River

Yellow GC
Golden Yellow GK
Yellow PGA
Yellow 5GK
Golden Orange G
Golden Orange 3G
Brilliant Orange RK
Brilliant Pink 2R
Red 6B
Red FBB
Red RK
Violet 6B
Violet 4R
Blue GF
Blue GCD
Blue RS
Dark Blue BO
Navy Blue RA
Brilliant Green BF
Brilliant Green 3G
Olive 2B
Olive 2R
Olive S
Brown BG
Brown BR
Brown GR
Brown RV
Black 2B
Black DRB

the tank to the neutralization compartments as needed. The unslaked lime residue is dumped several hundred yards from the treatment plant. Lime consumption may approach 10 tons per working day.

The neutral liquid flows from the neutralization basin into a 16,000,000-gallon lake where suspended color particles, calcium sulfate, and excess lime settle out. Capacity of this sedimentation basin can be increased to 29,000,000 gallons by raising the overflow level. If trouble arises in the handling of the effluent, the overflow from the sedimentation basin can be shut off. Several weeks would be required to fill the remainder of the basin; meanwhile the problem could be evaluated and corrections made.

When the effluent flows over the restraining barrier from the sedimentation basin, it falls into a pipe which leads to the 4,000,000-gallon aeration basin. Walls of this basin are asphalt and the floor is of fine gravel. Rows of pipes along the floor bubble air up through the effluent, effectively aerating it. A small portion of the effluent from the digester is circulated through the aeration basin to promote aerobic digestion.

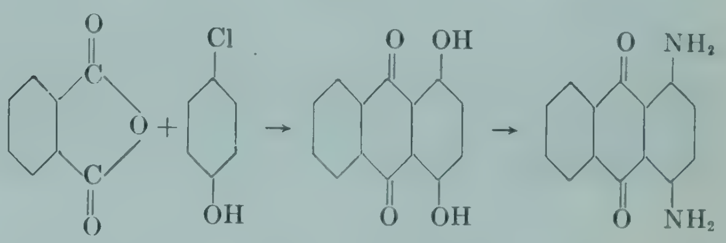
Finally, the effluent is chlorinated in an asphalt-lined tank, with wooden baffles for thorough mixing. A concrete duct leads several hundred feet from the chlorination tank to a small pond. Here, fish are raised to demonstrate to the neighbors that the effluent is harmless. Actually, the discharge will be of higher purity than the Toms River itself, which is highly colored by cedar swamps and has a fairly low (4.5 to 5.5) pH. The effluent is continuously sampled at all stages of treatment.

Organic Reactions in Great Variety Are Carried Out at Toms River

Temperatures varying from below 0 to over 500° F., and pressures ranging from 29 inches of vacuum to over 600 pounds gage are encountered in the various reactions. Besides about 35 dyes normally produced (Table III), many intermediates are made and stocked. Equipment flexibility is necessary for such a variety of products and processes (Figure 1). The capacity of 4,000,000 pounds of dyestuffs a year requires about 22,000,000 pounds of various raw materials. Chief among these are sulfuric acid, caustic soda, hydrochloric acid, phthalic anhydride, ammonia, benzene, nitrobenzene, glycerol, and alcohol.

Typical of the many anthraquinone vat dyes produced at Toms River is Cibanone Brown BR (Figures 2 and 3), a carbazole derivative of anthraquinone. It is produced from two intermediates that are also made and kept in stock, 1-chloroanthraquinone and 1,4-diaminoanthraquinone.

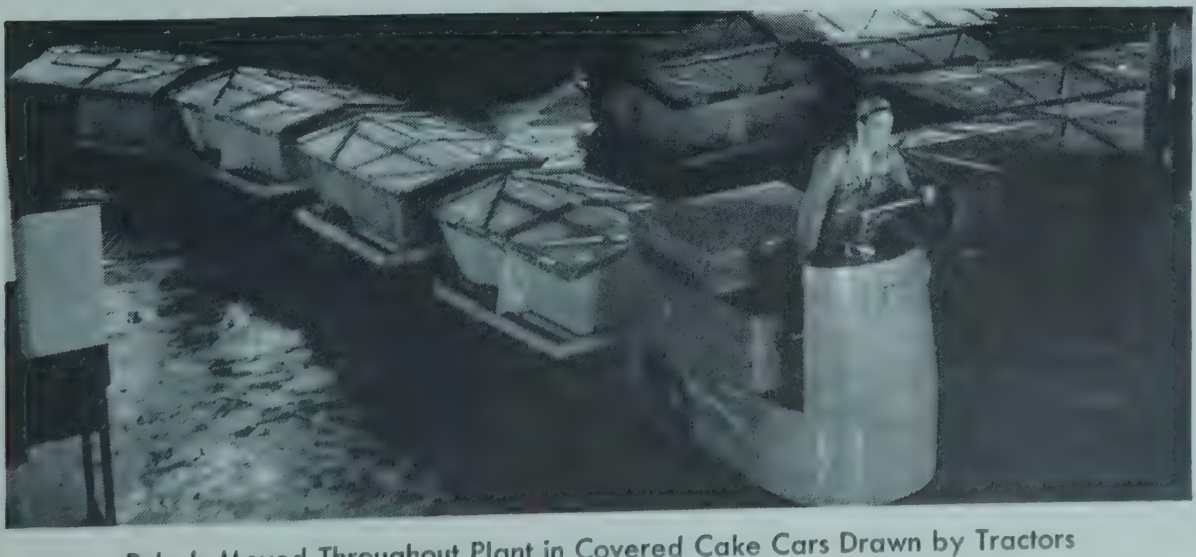
Phthalic Anhydride Condensed with *p*-Chlorophenol Makes Quinizarin for Amidation to 1,4-Diaminoanthraquinone



Sulfuric acid is charged into a 500-gallon enameled reactor (*10E*) from a measuring tank (*19E*); then boric acid is added, followed by phthalic anhydride from a drum suspended from a chain hoist. At 60° C. *p*-chlorophenol is added. By means of a Dowtherm heating system the reaction is heated to 194° C. over 5 hours and held for 7 hours to complete condensation. The charge is then blown through a blow leg with compressed air, into a 4000-gallon tank (*22E*) lined with acidproof brick (*17E*) and equipped with a lead-coated steel agitator and a lead-lined top, containing cold water. Quinizarine precipitates upon this drowning. Hot water at 80° C. is added to the suspension, and the mixture is heated to 130° C. with open steam. It is held at that temperature for 3 hours. After further dilution with water the suspension is blown with compressed air to the third floor, where it is filtered and washed acid-free with hot water on a wood filter press (*14E*). The quinizarin is dried in either air (*11E*) or vacuum ovens (*4E*).

Yield is about 145 pounds of quinizarin for each 100 pounds of *p*-chlorophenol. The purity of the product varies with the yield and can be raised to as high as 90 to 95% by sacrificing yield. The chief adulterants are purpurin and 2,7-dichlorofluoran in small percentages, and they are not removed. This quinizarin is amidated with 18% aqueous ammonia and sodium hydrosulfite, including some leuco-1,4-diaminoanthraquinone from a previous charge. The ammonia is run into the reaction kettle from a measuring cylinder (*19E*). The reaction takes place in a 750-gallon mild steel vessel (*22E*). The mixture is heated from room temperature to 90° C. over 5 hours and held at that temperature, under 30 to 45 pounds gage pressure, for 2 hours. Microscopic examination of the reaction mixture should show no crystals of leuco quinizarin but only the brownish crystals of leuco-1,4-diaminoanthraquinone. This test is carried out in the control laboratory.

The reaction mixture is cooled to 20° C. and blown to a suction filter (*23E*) on the third floor with compressed air. It is washed ammonia-free with cold water and dried in a vacuum chamber dryer (*4E*) under 29 inches of vacuum at 90° C. Yield is 91% of theory.



Pulp Is Moved Throughout Plant in Covered Cake Cars Drawn by Tractors

Intermediates Can Be Purified by Sublimation

Vacuum sublimer is cooled by outside water spray and jacketed inner cylinder

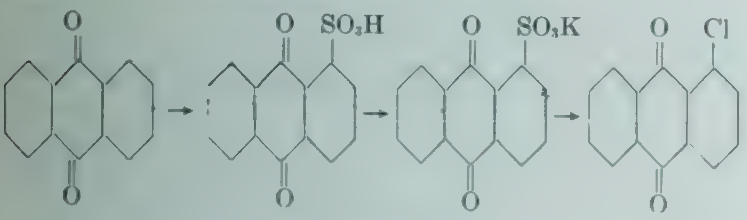
Dry Powder Blending

Horizontal ribbon powder mills in standardization building are charged from silos carried by special fork trucks. Silos or mills can be filled from grinding mills on floor above through flexible hose connections

In the solvent building, the leuco-1,4-diaminoanthraquinone is oxidized in a jacketed 750-gallon steel kettle (*22E*). The leuco intermediate is added to nitrobenzene at room temperature, with some piperidine as a catalyst. The reaction is heated slowly to 150° C. It is stirred at that temperature until control tests show that the reaction is complete.

A sample of leuco-1,4-diaminoanthraquinone dissolved in pyridine gives a dirty olive color, while the oxidized compound produces a clear, reddish blue solution. The test sample is compared with standards for evaluation. When the reaction is complete the charge is blown into a rotary vacuum dryer (*21E*) with inert gas. The solvent is vacuum distilled and recovered through a steel shell- and tube-condenser (*6E*) and a coil after-cooler (*25E*). The yield of 1,4-diaminoanthraquinone is 96% of theory. The finished intermediate usually contains a small amount of 1-hydroxy-4-aminoanthraquinone and about 1% of ash.

Sulfonation and Chlorination of Anthraquinone Leads to 1-Chloroanthraquinone



A mixture of new and recovered anthraquinone is sulfonated with 20% oleum in the presence of mercuric sulfate. The oleum is fed from a steel measuring tank (*19E*) into the cast-iron sulfonator (*18E*). Mercuric sulfate is added and dissolved by agitation at 50° to 60° C. for a half hour. Anthraquinone is charged from chain-hoisted drums. The mixture is heated to 120° C. over an hour and a half. After 4 hours at this temperature, about half the anthraquinone has been sulfonated.

Compressed air then blows the sulfonation mass into a 4000-gallon, acidproof brick-lined precipitation kettle (*17E, 22E*). Hot wash water from previous batches is run slowly into the hot sulfonation mass, with agitation from a large, heavy-duty, anchor-type stirrer. When the mass becomes too thick for efficient agitation, the stirrer is raised until it just clears the surface of the charge. Wash water addition is continued as the agitator works the water into the heavy mass from above. The stirrer is lowered into the mass as rapidly as the viscosity will permit, until it has once again reached the bottom of the tank.

Unreacted anthraquinone is filtered out in a brick-lined suction filter (*17E, 23E*) and washed acid-free. The filtrate is collected in a brick-lined receiver (*17E, 22E*) where addition of concentrated potassium chloride solution precipitates anthraquinone-1-potassium sulfonate. This precipitate is filtered on a brick-lined suction filter and washed with 0.5% potassium chloride solution. About 50% of the anthraquinone charged is actually sulfonated.

Chlorination to 1-chloroanthraquinone is carried out in a 3000-gallon brick-lined kettle (*17E, 22E*) heated by open steam through a porcelain inlet. The anthraquinone-1-potassium sulfonate is charged in paste form, and 1500 gallons of water are added. The proper volume of hydrochloric acid is run in from a measuring

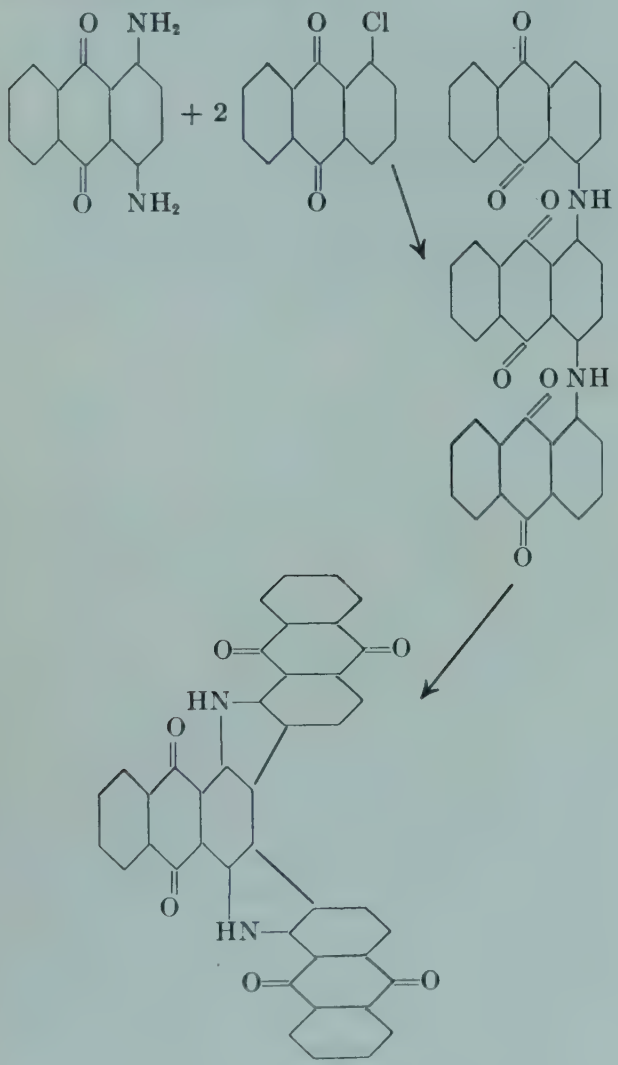
Solvent Recovery by Vacuum Distillation

A battery of rotary vacuum dryers (Venuleths) is flanked by condensers, coolers, and receivers tank (*19E*). After heating to 100° C., sodium chlorate is added in solution over about 16 hours. Temperature is held at 100° C.

A test for completion of the reaction is carried out by the control laboratory. A sample of the reaction mixture is filtered, and an excess of chlorate solution is added to the filtrate. If a yellow precipitate appears on boiling, chlorination is not yet complete and more chlorate is needed. The filtrate from another sample is made alkaline with sodium hydroxide. If unchlorinated anthraquinone-1-sulfonate is present, addition of sodium hydrosulfite will produce a red color. If no exposed iron is present, chlorination usually can be completed in less than 24 hours. If exposed metal or metal salts are included, the reaction will stop at 70 to 75% of completion.

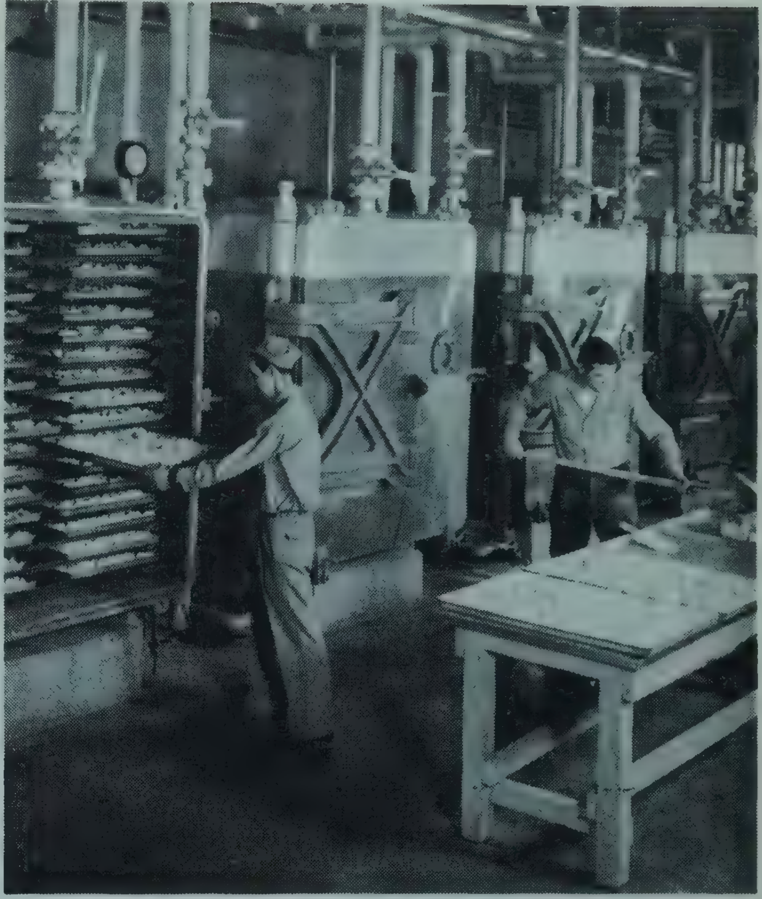
When the reaction is over, the chlorinator is filled to capacity with water. The product is filtered at 80° C. on an acidproof brick–lined suction filter (*17E, 23E*) and washed acid-free with hot water. It is dried in an air dryer (*11E*). Yield is approximately 94% of theory.

Intermediates Are Condensed to Trianthrimid for Carbazolation to Brown BR



In a glass-lined reactor (*10E*), 1-chloroanthraquinone and 1,4-diaminoanthraquinone are condensed to form the trianthrimid of Brown BR, 1,4-(dianthraquinonylamino)-anthraquinone. Nitrobenzene is used as the solvent, so the reaction must be carried out in the process building equipped to handle toxic and flammable solvents. Sodium acetate and soda ash are added to neutralize and buffer the hydrogen chloride given off in the condensation. A colloidal copper catalyst is included in this reaction.

The nitrobenzene is run into the reaction vessel from a measuring tank (*19E*), and 1-chloroanthraquinone, 1,4-diaminoanthraquinone, sodium acetate, soda ash, and the copper catalyst are added. The batch is heated to 210° C., and held for 10 to 15 hours. Compressed inert gas then blows the contents of the kettle to a rotary vacuum dryer (*21E*) where the nitrobenzene is distilled off and recovered. The dry trianthrimid is ground in a micropulverizer (*12E*) and boiled in dilute hydrochloric acid to remove salts. This purification step is carried out in an acidproof brick–lined kettle (*17E, 22E*). The purified trianthrimid is filtered and washed in a filter press (*14E*) and dried in a vacuum chamber dryer (*4E*).



Vacuum Chamber Dryers

These dryers are used for heat-sensitive substances; stainless steel trays are placed on steam-heated shelves

Carbazolation is effected in a glass-lined jacketed kettle (*10E*). Pyridine is fed into the tank from a measuring tank (*19E*). Aluminum chloride is poured in from a chain-hoisted drum, and the temperature is held between 100° and 130° C. while the trianthrimid is added. The temperature is held at 135° C. until a sample taken from the melt shows the same appearance as a standard sample. The melt sample is boiled with 30% sodium hydroxide, diluted, and filtered. The residue is dried on a porous plate and compared with the standard.

When the reaction is complete, compressed inert gas blows the mixture into a 4000-gallon acidproof brick–lined vessel (*17E, 22E*) containing caustic soda solution charged from a measuring tank (*19E*). Pyridine is distilled off with direct steam and recovered in a liquid-liquid extraction column (*9E*). A solution of sodium hypochlorite is run in from another measuring tank (*19E*), and the slurry is boiled for about an hour. An excess of sodium bisulfite is added to remove excess bleach, and the slurry is filtered in an iron filter press (*14E*). The Cibanone Brown BR is washed to neutrality and standardized.

Standardization Includes Treatment of Chemically Finished Dye to Ensure Proper Physical Form

Manufacture of anthraquinone vat dyes has probably changed very little over the past 30 years, but great progress has been made in solving the problems of putting the dye in the proper form for easiest and most economical use. The physical form of anthraquinone vat dyes affects markedly the ease of vatting and affinity for the fiber (*5*). Dyes separated in crystalline form from

Laboratory Where Dye Colors Are Tested in Small Stainless Steel Vats

organic solvents are usually difficult to vat. Poor shades and wasted material may result. Different treatments have been developed to prepare dyes for different end uses.

Only 12 to 15% of vat dye production is sold as dry powders. The overwhelming majority of the output is sold in paste form in varying concentrations, from 10 to 30% dye. Surface-active agents, humectants, or other additives may be included.

Dissolving the crystalline dye in concentrated sulfuric acid and reprecipitating by drowning in water is a standard and effective method of improving the vatting and dyeing properties. Treatment with oxidizing agents such as sodium hypochlorite or dichromate solution near boiling, for an hour or more, with vigorous mechanical agitation markedly improves the shades of many dyes.

The standardization of dye pastes usually consists of conventional paste grinding, with the addition of conditioning agents to regulate the fluidity of the paste. Aryl sulfonic acid derivatives are among the conditioning agents used. Glycerol is added to printing pastes. The shade and strength of the pastes are standardized in mixing kettles. The product is then strained into drums ready for shipment.

When the chemical synthesis of Brown BR is complete, the pulp is charged into stainless steel 1500-gallon kettles and the concentration is adjusted approximately. It is ground in a micropulverizer until the desired particle size and consistency are attained and then returned to the pasting kettle. Samples are examined in the laboratory, and the strength and shade are finally adjusted. The finished paste is put through a 200-mesh screen into drums for shipping.

Powders are also ground in a micropulverizer, but they are blended in horizontal ribbon powder mills (*15E*).

Quality Control Includes Laboratory Scale Dyeings

Every batch of dyestuff turned out at Toms River is subjected to actual use tests in the laboratory. Yarn or cloth is dyed on a laboratory scale in stainless steel dye beakers. The dyed fibers are checked for shade and strength and for fastness to light, washing, and crocking. Particle size is checked by microscopic examination, filter, and sieve tests. Filter tests with cheesecloth or filter paper determine the amount of difficultly soluble residue. Crystal structure is studied with microscopes.

Research Should Be Directed Toward Making Anthraquinone Vat Dyes Less Expensive, Easier on Fabric, and Brighter

More than 50 years after their discovery, there is still much room for improving anthraquinone vat dyes. Although these are the fastest growing dyes and least affected by the present slump in the textile industry, they are expensive and not yet comparable in brightness with other classes of dyes that do not, however, possess their fastness. The application of vat dyes requires considerable skill. This would be another fruitful field for research.

Some anthraquinone dyes, especially those used for the production of lemon or greenish yellow shades with the maximum light fastness, show a pronounced tendering effect on the dyed fiber. Elimination of this defect and development of light shades having good light fastness is one of the most important problems facing the dye chemists.

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(2) Thorpe and Ingold, "Vat Colours," p. 175, London, Longmans, Green and Co., 1923.
(3) U. S. Dept. Commerce, OTS, Washington 25, D. C., FIAT Final Rept., **1313**, Vol. II, 1949.
(4) U. S. Tariff Commission (Supt. Documents, Washington 25, D. C.), "Synthetic Organic Chemicals—U. S. Production and Sales," 1947–1952.
(5) Venkataraman, "Chemistry of Synthetic Dyes," Vol. II, New York, Academic Press, 1952.

Processing Equipment

(1E) A. O. Smith Co., Milwaukee, Wis., custom-built autoclave, mild steel, clad with 316 stainless steel, 500 to 2500 gallons.
(2E) Blaw-Knox Co., Pittsburgh, Pa., custom-built sublimer, 304 stainless steel–clad mild steel.
(3E) Chemical Engineering Catalog, Reinhold, New York, 1952–54, Croll-Reynolds Co., steam-jet Evactor, **321-JJ**, three-stage, cast-iron, 304 stainless steel nozzle, hard bronze throat.
(4E) *Ibid.*, J. P. Devine Mfg. Co., No. **27** vacuum chamber dryer.
(5E) *Ibid.*, Dowtherm Div., Dow Chemical Co., Dowtherm A.
(6E) *Ibid.*, Doyle and Roth Manufacturing Co., Shell-and-tube condenser, **2081-5E**, 304 Stainless steel.
(7E) *Ibid.*, Haynes Stellite Co., Hastelloy B and C.
(8E) *Ibid.*, La Bour Co., centrifugal pump Type **BG**, vertical, packingless, self-priming, size 12.
(9E) *Ibid.*, Otto H. York Co., York-Scheibel multistage extractor, 9-stage, 3-inch diameter, 304 Stainless steel.
(10E) *Ibid.*, Pfaudler Co., custom-made glass-lined reaction kettle.
(11E) *Ibid.*, Proctor and Schwartz, two-compartment truck dryer, hot-air circulation, automatic temperature control (10 ft. × 12 ft. × 9 ft. 6 inches).
(12E) *Ibid.*, Pulverizing Machinery Co., Mikro-Pulverizer **3TH**.
(13E) *Ibid.*, Roots-Connersville Blower Div., Dresser Industries, inert gas generator, 6000 cubic feet per minute, blower type **AF**, gas pump type **XA**.
(14E) *Ibid.*, T. Shriver and Co., plate-and-frame filter press, three-eyed, top-center feed, washing-type open delivery, hydraulic closing device.
(15E) *Ibid.*, Sprout-Waldron and Co., Style **B** horizontal ribbon-and-paddle agitator batch blender.
(16E) *Ibid.*, Worthington Corp., Type **HBV** dry vacuum pump, single horizontal feather valve, piston displacement 22 by 9 inches, 300 r.p.m.
(17E) Chemsteel Construction Co., Pittsburgh, Pa., acidproof brick lining.
(18E) Lynchburg Foundry Co., Lynchburg, Va., custom-built, cast-iron reactor.
(19E) Struthers Wells Corp., Warren, Pa., custom-built measuring cylinder 250 gallons.
(20E) *Ibid.*, custom-built mild steel pressure filter.
(21E) *Ibid.*, custom-built mild steel rotary vacuum dryer.
(22E) *Ibid.*, custom-built mild steel reaction kettle.
(23E) *Ibid.*, suction filter box, mild steel, 100 and 150 sq. ft.
(24E) *Ibid.*, Dowtherm liquid heater, 5,000,000 B.t.u./hour.
(25E) Wall-Derkiss Fabricators, Linden, N. J., coil-type aftercooler.

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SPECIALTY SOAPS

KENNETH M. REESE, *Assistant Editor*

in collaboration with

RALF B. TRUSLER AND IRENE T. BUGAS
The Davies-Young Soap Co., Dayton, Ohio

HOW far the use of soap reaches into antiquity is a matter for conjecture; probably the earliest reference is found in Babylonian cuneiform tablets of the third millennium B.C. The first known soap formulation appears in Sumerian records of about 2250 B.C. (*5*); it specifies 1 part of oil to $5^1/_2$ parts of alkali (probably in the form of ash). Soap is mentioned in the Bible, and a well equipped factory was found at Pompeii. An early method of manufacture, according to Pliny (first century A.D.), was the boiling of causticized wood ashes with goat tallow. The soft potash soap thus formed could be changed to a hard soda soap by treating the paste repeatedly with salt.

Soap was known in Italy and Spain in the 8th century A.D., and had reached France by the 12th century. In the late 14th century it was being used in England, and in 1622 James I granted a soapmaker a monopoly allowing manufacture of 3000 tons a year.

Soap had become a commercial item long before anything was known of the chemical nature of its manufacture. In 1823 the French chemist, Chevreul, published his well-known researches in fats and oils (*4*). These data, together with the earlier development of the Leblanc soda process in about 1791, first provided the chemical technology and raw material availability from which present-day soap manufacture has grown.

A household art until well after 1800, soapmaking in the U. S. hit its peak in the war year, 1944, when over 4 billion pounds of soap were produced. Synthetic detergents have successfully invaded the field since, but soap as such is still a big enterprise; an estimated 1.984 billion pounds were made in 1953 (*3*).

The American Society for Testing Materials defines soap as "the product formed by the saponification or neutralization of fats, oils, waxes or rosins or their acids with organic or inorganic bases" (*2*). This definition today covers a multitude of products. Soap usage is no longer limited to cleaning nor are all commercial soaps metallic salts of the fatty acids. Aluminum, magnesium, and calcium soaps are among those used in noncleaning applications. Printing inks, textile waterproofing, and thickening of lubricating oils are representative end uses. Materials like ammonia and triethanolamine react with fatty acids to form soaps used in dry cleaning, household cleaners, and cosmetics.

The Davies-Young Soap Co. Is a Leader in U. S. Specialty Soap Production

The manufacture of soap and sanitary specialties for industrial cleaning and maintenance, while constituting less than 3% of the total U. S. output of soaps and detergents—4.118 billion pounds in 1953 (*3*)—is an important segment of the soap industry. In this field, The Davies-Young Soap Co. of Dayton, Ohio, is probably the largest manufacturer.

The company's precursor, the J. P. Davies Co., originally produced tallow and lard oils for lubrication and oil lamps. The rapidly growing invasion of this field by petroleum products, however, led the company to shift in 1888 to the making of bar soap, and in 1892 it became the first to market chip soap in barrels for use in commercial laundries. In 1912 the company began making dry cleaning specialities, most of which had been imported from England and France prior to that time.

J. P. Davies Co. became Davies-Young in 1914, and potash soaps, still making up a large part of the company's production, became the staple item of manufacture. Since that time, the sizes and types of industrial surfaces which must be cleaned have grown rapidly. The company has grown in a like manner, and in 1949, in the interest of greater productive capacity and versatility, moved from the quarters occupied since 1914 to the present $1,500,000 Dayton plant.

The keystone of specialty soap manufacture is versatility. Davies-Young turns out 77 standard soap products, and this list is swelled to 150 by the inclusion of more highly specialized, less frequently produced items. These products are marketed to industry in bulk or under private brand, only a negligible amount finding its way into the home. They are produced as liquids, pastes, and bars, and shipping containers have varied from 1-pound jars to tank cars. A representative list of products would include scrub and toilet soaps, surgical, disinfectant, and insecticidal soaps, shampoo soaps, lubrication soaps, dry cleaning soaps and spotters, and degreasers.

It is difficult to arrive at an accurate figure for plant capacity because of the large number of products, the different manufacturing times associated with them, and the variability of product scheduling with consumer demand. Suffice it to say that Davies-Young's output is millions of pounds monthly. The cost distribution per pound of product is somewhat unusual. If cost of sales is broken down to costs of raw materials, packaging, labor, and overhead, labor and overhead make up only 15% of the total.

There are in the soap industry companies known as "converters." Such companies buy concentrated soaps in bulk from primary producers and alter them in a number of different ways to fulfill various customer requirements. The end uses of these and other soaps are often unknown to the manufacturer and not infrequently turn out to be quite unusual. One firm used a certain soap as a chemical reactant, and another product served as an air-entraining agent in concrete. For these reasons Davies-Young is reluctant to alter a soap formulation in any degree without also changing the name under which the product is sold. This policy is important because a rather high percentage of specialty soaps is processed by converters.

The bulk of the paste and liquid potash soaps produced in the United States is made by the semiboiled process, and this is the method most used by Davies-Young. In the semiboiled process, the exact amount of caustic or potash needed for complete saponification is heated with the oil or fat, using both closed and open steam. When saponification has started, mechanical agitation, steam, and cold water are used at the soapmaker's discretion to control the reaction. The process goes to completion in the kettle and the glycerol produced is retained in the soap.

The cold-made process is used by Davies-Young in the manufacture of bar soaps. This method employs continuous mechanical agitation and only enough heat to get the reaction started. The amounts of reactants used must be precisely calculated, because as soon as they are thoroughly mixed and saponification is well under way, the batch is run into frames where the process, promoted by the heat of reaction, goes to completion. Again, the glycerol produced is retained in the finished soap.

The chemical heart of these processes is the classical saponification reaction of caustic or potash with animal and vegetable fats and oils to produce sodium or potassium salts of the fatty acids and glycerol.

$$C_3H_5(OOC.R)_3 + 3KOH(\text{or }NaOH) \rightarrow 3K.OOC.R + C_3H_5(OH)_3$$

Soap Can Be Made from Many Different Fats and Oils

A number of naturally occurring fats and vegetable oils have been and are being used in soap manufacture. Davies-Young has used soybean oil, coconut oil, babassu oil, cottonseed oil, linseed oil, tall oil, tallow, and rosin, among others. All these materials are esters of fatty acids and the trihydric alcohol, glycerol.

$CH_2OCOC_{17}H_{35}$	$CH_2O.COC_{17}H_{35}$	$CH_2O.COC_{17}H_{35}$
$CHO.COC_{17}H_{35}$	$CHO.COC_{17}H_{35}$	$CHO.COC_{15}H_{31}$
$CH_2OCOC_{17}H_{35}$	$CH_2O.COC_{17}H_{33}$	$CH_2O.COC_{17}H_{33}$
Tristearin	Oleodistearin	Oleopalmitostearin

These examples show that the glyceride molecules may contain three radicals of the same fatty acid or radicals of two or three different fatty acids. The fatty acid radicals may be saturated (C_nH_{2n+1}) or unsaturated (C_nH_{2n-1}, C_nH_{2n-3}). Lauric acid, $C_{11}H_{23}COOH$, myristic acid, $C_{13}H_{27}COOH$, palmitic acid, $C_{15}H_{31}COOH$, and stearic acid, $C_{17}H_{35}COOH$ are the saturated fatty acids found most often in nature. Oleic acid, $C_{17}H_{33}COOH$, is the most important naturally occurring, unsaturated fatty acid (*6*).

The best cleansing soaps are generally derivatives of those fatty acids containing from 12 to 18 carbon atoms. Below 12 carbon atoms the surface action necessary to good detergency falls off, and above 18 carbon atoms water solubility at ordinary temperatures becomes too low. There are several commonly used tests that are helpful in evaluating a fat or oil both as to composition and the type of soap that it will make. The iodine number indicates the degree of unsaturation of the fat or oil. The titer test gives a measure of the proportions of mixed fatty acids present in the fat or oil. The saponification number indicates the proportions of the high and low molecular weight fatty acids present and thus the amounts of oil and alkali needed to make a given soap.

Generally speaking, the more unsaturated materials, which have higher iodine numbers, make softer soaps, and these soaps are more subject to oxidation darkening when exposed to air than are those made from the more saturated fats or oils. Titer, the temperature at which a molten sample of a fat or oil begins to crystallize upon cooling, gives a fair idea of the hardness of the soap that will be produced from the fat or oil at hand. If the materials are of the same family—several different soybean oils, for example—those having the higher titer will, as a rule, make the harder soap.

The fats and oils used at Davies-Young must meet definite specifications on receipt and are used as delivered, without further purification. Laboratory checks on moisture content and the percentage of unsaponifiable materials are made occasionally, but except for materials relatively new to the plant, it is seldom necessary to check titer, iodine number, and saponification number.

Fat and vegetable oil color can be important in soap manufacture because of its effect on the eye appeal of the finished soap. The company uses both a light and a dark soybean fatty acid and a light (cochin) and dark (manila) coconut oil. Lighter color in a given oil is, as a rule, evidence of a more highly refined material.

Which of the available oils are used in formulating a product depends largely upon cost, since many soaps can be produced from any of several different oils with approximately the same end results. The major saponification materials currently used by the company are coconut oil, soybean oil, soybean fatty acid, oleic acid (red oil), and tallow (Table I).

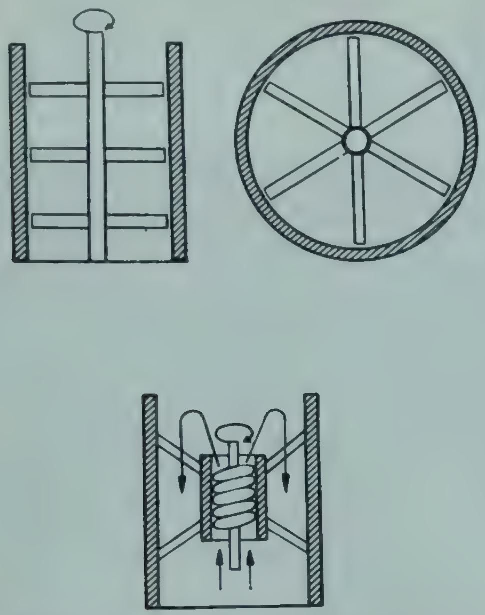


Figure 1. Paddle Type Agitator (Top) Crutcher Agitator (Bottom)

The direct saponification of fatty acids is used at Davies-Young to make soaps low in, or free of glycerol, and has also found use (when glycerol was not a factor) because of cost advantages. It has been possible from time to time to obtain by-product fatty acids, suitable for certain soaps, at a lower cost than for the parent vegetable oil. Fatty acids are not likely to supplant whole oils, however, because the glycerol produced and retained in the soap when the latter are used is of value. It improves the clarity of liquid and paste soaps and has an emollient effect—i.e., the soap "feels" better to the user.

Other Raw Materials Include Caustic, Potash, Solvents, Perfumes, and Coloring Agents

Commercial caustic and potash solutions (Table I) are the saponifying agents most used by the company. Certain organic amines are also used to some extent. Potassium soaps are, in general, softer than sodium soaps, although there are hard potassium soaps and soft sodium soaps. Potassium soaps are more soluble than their sodium counterparts; for this reason most liquid and paste soaps are of the potash type. The presence of sodium soaps may cause clouding in a liquid soap intended to be clear. It might also cause "figging," the appearance of hard, white nodules in a paste soap. Caustic is used straight or blended with potash in the making of bar soaps; proportions are set up so as to achieve the desired balance of hardness and solubility.

Process water comes from wells and is treated in two potassium chloride regenerated zeolite units, each of which has a capacity of 12,000 gallons between regenerations. Hardness content, largely calcium carbonate, runs about 410 p.p.m. before treatment and 34 p.p.m. after treatment. Dissolved solids are present after treatment largely as potassium carbonates and bicarbonates. The zeolite is regenerated with potassium chloride rather than sodium chloride because sodium salts in the process water would yield small amounts of less soluble sodium soaps which would tend to cloud the clear paste and liquid potash soaps being made.

Besides these basic raw materials, a number of other products are employed in relatively large amounts. Among them are petroleum naphthas, Stoddard solvent, epoxylated solvents, cresol, and xylene.

Many perfumes and coloring agents are used and are generally added in the kettle for paste and bar soaps and in the shipping containers for liquid soaps. Fine silica is used in the manufacture of abrasive soaps. Chelating agents like the sodium salt of ethylenediaminetetraacetic acid are used in liquid soaps to tie up residual calcium and magnesium in the form of soluble complexes, thus improving clarity. Various organic solvents go into dry cleaning soaps. Antioxidants such as 2,6-di-*tert*-butyl-4 methylphenol are used in many soaps to prevent the development of rancidity. Pine oil, hexachlorophene, and similar substances go into antiseptic and disinfectant soaps.

Production Revolves about the Soap Kettles

The heart of a soap plant is the kettle room. Davies-Young regularly operates about 20 soap kettles of varying sizes and designs (Table II). Most of these are provided with a means of mechanical agitation, and all are supplied with 100-pound-per-square inch steam, in closed coils, open coils, jackets and combinations of the three. All the agitation devices are driven by individual induction motors. Two general types of agitator (Figure 1) are used—paddles and crutchers. Paddles are mounted in opposed radial pairs on a shaft installed along the vertical center line of the kettle. Up to five such pairs are used. Speed of rotation is about 90 r.p.m.

A crutcher is a helical screw mounted on a shaft installed along the vertical center line of the kettle. The screw revolves inside a vertical, cylindrical steam jacket open at each end. The material being agitated is drawn upward by the action of the crutcher, so that flow is upward through the crutcher jacket and downward around the circumference of the kettle. If a kettle has crutcher type agitation, the entire kettle is generally referred to as a crutcher. Crutcher speed is about 250 r.p.m.

The soap kettles are highly interchangeable. It is the boast of the soapmakers that they can make just about any of the soaps produced in any of the kettles, providing the finished soap can be drained or pumped from the kettle, and this is very nearly true. Production considerations dictate, however, that certain kettles be used more or less regularly for certain groups of soaps, the usual dividing line being whether the product is liquid, paste,

Table I. Some Basic Raw Materials Used in Production of Specialty Soaps

	Coconut Oil	Soybean Oil	Soybean Fatty Acid	Oleic Acid (Red Oil)	Tallow
Properties (av.)					
Sapon. No.	252	190	198	198	195
Iodine No.	8.5	131	130	95	40
Titer, ° F.	22	22	24	5	44
Unsapon., %	0.25	0.5	3	2	4
Moisture, %	<1	<1	<1	<1	<1
Fatty acid compn., %					
Caproic	0.5	...	...	...	...
Caprylic	7.5	...	...	...	...
Capric	7	...	...	...	...
Lauric	47	...	...	...	...
Myristic	19	...	...	...	2
Palmitic	9	6.5	7	4	29
Stearic	2	4.5	4	5	24.5
Oleic	7	33.5	34	80	44.5
Linoleic	1	52.5	51	10	...
Linolenic	...	2.3	4	1	...

	Potash		Caustic	
	Recd.	Used	Recd.	Used
° Bé.	49	40	50	33
KOH/NaOH, %	48.9–49.85	38.4	45.0–49.5	28.8
Impurities (av.), %				
NaOH	0.3	...	...	..
K_2CO_3	0.2	..	...	..
KCl	0.7	..	...	..
Na_2CO_3	...	..	0 15	..
NaCl	...	..	1.0	..
Other[a]	>0.01	..	>0.025	..

[a] Fe_2O_3, Al_2O_3, SO_3, SiO_2, CaO, MgO, Ni, Ti, Cu, Pb, As.

Kettle Room on Second Floor of Manufacturing Building

Kettle outlets are on first floor

Interior of 8800-Gallon Soap Kettle

Note agitator blades and steam coils

or bar. When shifting from one soap to another using the same kettle, the major consideration is color. If the change is from a product formulated with a dark vegetable oil, for instance, to one formulated with a lighter oil, the kettle must first be washed, using water and open steam. Several washes are used; the first wash water, containing most of the residual soap, is saved and recharged to the kettle the next time a soap of the same type is to be made.

Raw Materials Handling Equipment Must Be Flexible

The flow of raw materials in a specialty soap plant is very important (Figure 2). The large amounts of liquids that must be moved require, in the interest of power economy, that gravity flow be utilized wherever possible. Also, the large number of products manufactured, and the versatility that must be built into the plant make it essential that alternative means of routing each major raw material be made available.

Most of the plant's large quantity raw materials are received in tank cars, from which they are centrifugally pumped into bulk storage. Two outdoor vertical cylindrical tanks with a combined capacity of 18,000 gallons hold the potash; caustic is stored in two similar tanks, combined capacity 17,000 gallons. Soybean oil, and light and dark soybean fatty acids are held in six outdoor vertical cylindrical tanks with a combined capacity of 25,000 gallons. All these tanks are equipped with internal steam heating coils. Four coconut oil bulk storage tanks, total capacity 27,800 gallons, are located in a heated building. Indoor storage is necessary because the prolonged use of heating coils that might be necessary if coconut oil were stored out of doors would result in "burned" (discolored) oil.

From bulk storage, potash and caustic go directly to make-up tanks on the third floor of the manufacturing building. Here they are reduced from shipping concentrations, 49° Bé. (potash) and 50° Bé. (caustic) to 40° and 33° Bé., respectively. At these strengths, equal weights of potash and caustic have approximately equal hydroxide values; this makes it simple for the soapmaker to interchange them when necessary.

Soybean oil and soybean fatty acids from bulk storage may go to production storage on the first floor of the manufacturing building, to the metering system, and thence into the kettles or to the third floor make-up tanks. Coconut oil may go to either production storage or the make-up tanks. There are four rectangular, open-top production storage tanks which may be used interchangeably for the various oils and fatty acids. They are provided with internal steam coils, have a combined capacity of 4900 gallons, and are charged with the same pumps that are used to empty the tank cars.

Also located on the first floor are two oleic acid tanks, combined capacity 5900 gallons, and two tallow tanks, total capacity 2100 gallons. These tanks are rectangular, open-topped, and have internal steam heating coils. Tallow is delivered in drums, melted in a steam room on the second floor, and drained through a heavy wire screen with openings about $^1/_4$-inch square into the storage tanks.

From production storage, coconut oil, and soybean oil and fatty acid may go to the third floor make-up tanks or directly to the meters. Tallow always goes to the make-up tanks. All these materials are centrifugally pumped, excepting tallow, for which a horizontal, duplex, steam-driven pump is provided.

From make-up, the raw materials are either charged through the metering system or weighed and gravity fed into the kettles on the second floor. Tallow, because of its viscosity, and caustic, because of the relatively small quantity used, are never routed through the meters. One meter is provided for all the vegetable oils and fatty acids and one for potash. The vegetable oil metering system can be blown out with steam when necessary.

The meters (50 gallons per minute) are carbon piston type, positive displacement units working under a maximum pressure of 125 pounds per square inch. Bellows type thermal units compensate the meter readings for temperature induced changes in

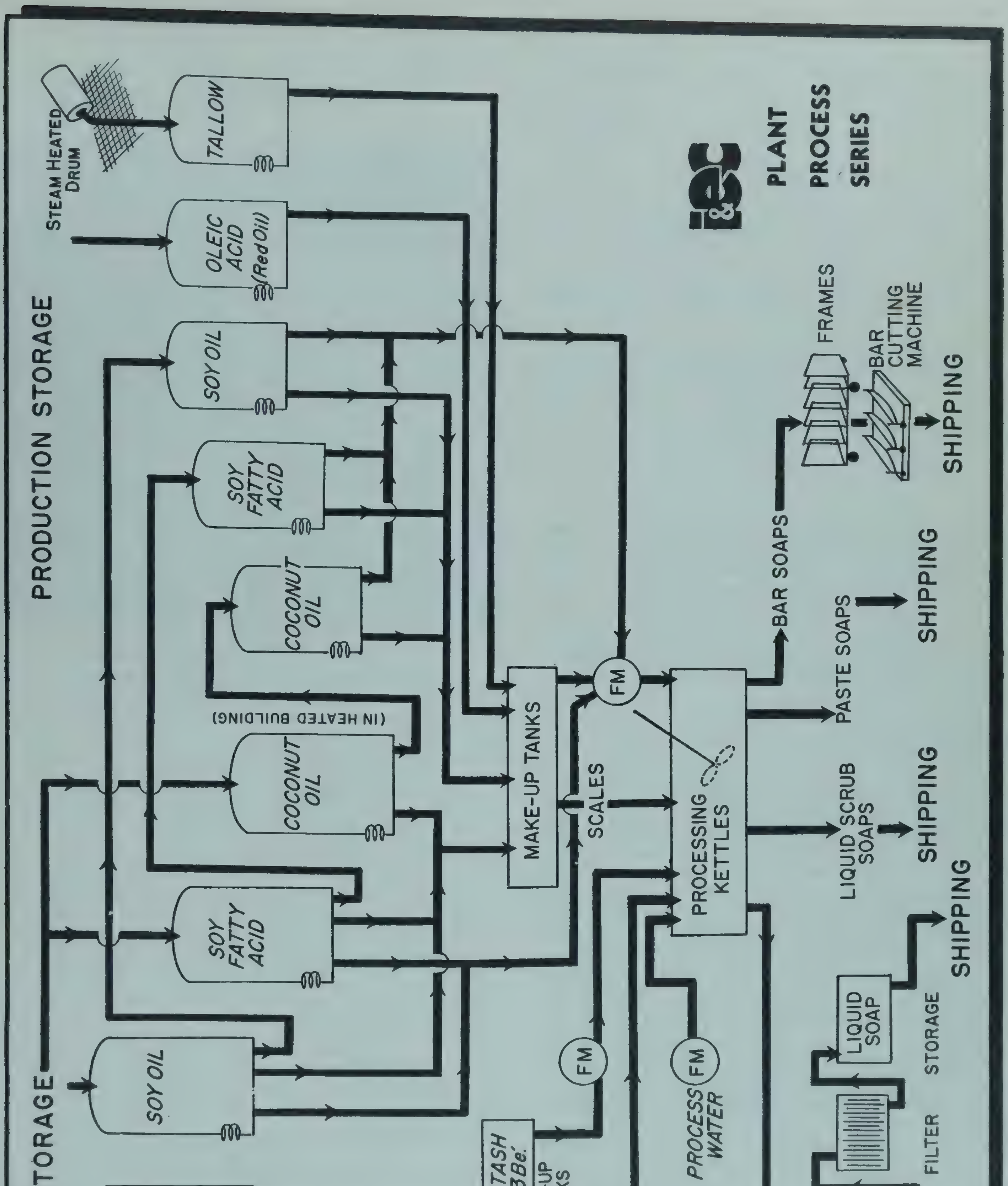

BULK STORAGE
PRODUCTION STORAGE
STEAM HEATED DRUM
TALLOW
OLEIC ACID (Red Oil)
SOY OIL
SOY FATTY ACID
COCONUT OIL
(IN HEATED BUILDING)
COCONUT OIL
SOY FATTY ACID
SOY OIL
POTASH 50Bé'
CAUSTIC 49Bé'
STEAM
CAUSTIC 40Bé'
MAKE-UP TANKS
POTASH 33Bé'
MAKE-UP TANKS
FM
PROCESS WATER
FM
MAKE-UP TANKS
SCALES
FM
PROCESSING KETTLES
BAR SOAPS
FRAMES
BAR CUTTING MACHINE
SHIPPING
PASTE SOAPS
SHIPPING
LIQUID SCRUB SOAPS
SHIPPING
LIQUID SOAP
AGING AND SETTLING TANK
LIQUID SOAP
COOLING COILS
FILTER
LIQUID SOAP
STORAGE
SHIPPING
I&EC
PLANT PROCESS SERIES

Figure 2. Flow Sheet for Production of Specialty Soaps at Davies-Young Soap Co., Dayton, Ohio

Table II. Representative Soap Kettles

Kettle[a] No.	Diam. × Depth, Feet	Max. Batch Vol.[b], Gal.	Agitation		Heat Supply	Products	Remarks
			Type	Motor			
1	10 × 15	4400	5 pairs radial paddles	10-hp. induction, 4-speed reduction unit	Steam coils, closed and open	Liquid scrub soaps and paste soaps	Closed top, observation hatch; lower 10 ft. cased in wood; 4-inch bottom outlet
2	10 × 15	4400	None	.....	Open steam coils	Liquid toilet soaps	Closed top, observation hatch; interior ladder; 2-inch bottom outlet
	4 × 6	330	Crutcher in 24 × 30 inch jacket	15-hp. induction	Lower 36 inches steam jacketed; crutcher steam jacket; open steam coils	Paste soaps	Closed top, observation hatch; cone-bottomed; 8-inch bottom outlet
4	4 × 5	280	Crutcher in 36 × 36 inch jacket	2-hp. induction	Steam coils closed and open; kettle jacket; crutcher steam jacket	Bar soaps	Closed top, observation hatch; cone-bottomed; 3-inch bottom outlet
5	4.16 × 11	550	Crutcher in 24 × 30 inch jacket	5-hp. explosion-proof induction	Lower 48 inches steam jacketed; crutcher steam jacket	Dry-cleaning formulations	Closed top, observation hatch; cone-bottomed; 3-inch bottom outlet

[a] All kettles are steel, cylindrical, and vertically installed.
[b] Kettles not filled to capacity because of danger of foaming and overflow.

liquid volume up to $3^1/_2\%$, based on a reference temperature of 77° F. The meters are not so accurate a measure as weighing and are not used when measurement must be precise. Neither are they used to charge the larger kettles, since they would be tied up for extended periods of time during which several smaller kettles could be charged. The metering system is somewhat unusual in this type of plant and is still open for improvement, but the company feels that on the whole it is profitable and can be made more so.

The Soapmaker's Experience Is His Best Instrument

Batch soapmaking at Davies-Young is an art. Little instrumentation is used; much depends upon the skill of the soapmakers, who in this instance have an average of about 20 years of experience to draw upon. The progress and condition of the batch are checked by the eye and by touch until it is nearly finished, when laboratory checks are made on alkalinity or acidity and solids content. Occasionally, when in a hurry, a soapmaker will discharge a batch of soap before the laboratory check is completed. These batches are seldom out of limits; it is not uncommon for the soapmaker to predict alkalinity, for instance, within 0.1%.

While each soapmaker has his own personal techniques, certain basic procedures are axiomatic in the production of semiboiled and cold-made soaps. These may be logically separated into those applying to liquid soaps, paste soaps, bar soaps, and dry cleaning soaps.

The starting point is the production order, which gives the soap formulation and the size of the batch to be made. Formulations are accurately calculated, so that only a very small excess of saponifiable or alkaline materials goes into the kettle. Although the oils used may vary according to source in the types and proportions of fatty acids present, their composition is consistent enough to permit calculation of standardized yield data (Figure 3). Curve II in Figure 3 can be used for most of the commonly employed vegetable oils, such as soybean, cottonseed, and corn with a maximum error of about 1%.

Liquid Soap Finished at 40% Total Solids

The formulation for a 40% liquid soap is:

	Pounds
Coconut oil (manila)	12,672
Potash (40° Bé.)	8,100
Water	15,000

This soap is made in kettle No. 2 (Table II). When finished, it will contain 40% total solids (soap plus glycerol) and will have a free alkalinity of 0.15 to 0.25% as potassium hydroxide. The soap will generally be used as an industrial toilet soap.

The coconut oil is pumped from production storage to the third floor, where it is weighed and gravity fed into the kettle. Potash is pumped from bulk storage to the third floor where it is diluted to 40° Bé., weighed, and gravity fed into the kettle. At the same time, two thirds of the water requirement is metered into the kettle. The open steam is then turned on, and the batch is cooked for 6 to 8 hours. Reaction temperature, not available to the operator, is about 212° F. Agitation is provided by the steam and by convection currents arising from the heat of reaction. During the cooking period the soapmaker controls the

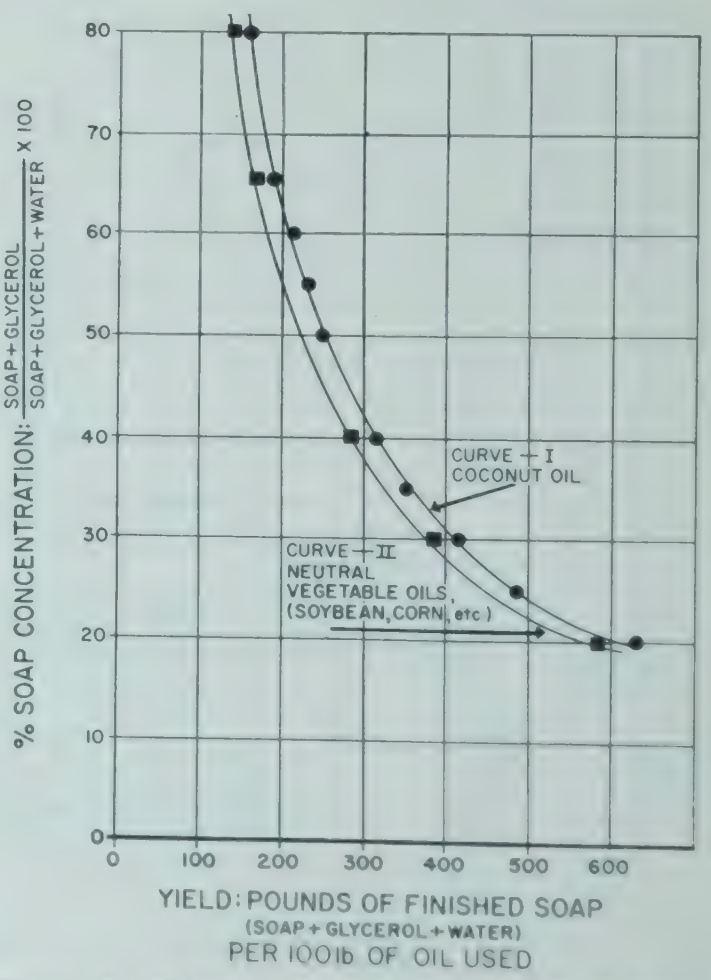


Figure 3. Calculation of Standardized Yield Data for Soap Production

reaction by judicious use of the steam and water; the remaining third of the water requirement will have been made up by the time the batch is about finished. Foaming, indicating an excessive speed of reaction, is held at a level which the operator has learned through experience to be most favorable.

Interior of Crutcher, Showing Agitator

Helical screw revolves inside a steam jacket

When the batch is nearing completion, the soapmaker begins periodically to drip phenolphthalein from a medicine dropper into the kettle as an alkalinity check. Color changes show up well on the white, foaming surface of the batch. Finally, when the soap appears to be finished, a sample is dipped out of the kettle for laboratory analysis of solids content and alkalinity.

Liquid Toilet Soaps Are Aged and Filtered

When the laboratory reports the batch to be within the desired limits, it is pumped from the kettle through a bottom outlet by a horizontal, duplex, steam-driven pump to one of three vertical, cylindrical outdoor tanks with a combined capacity of 15,300 gallons. These tanks are provided with internal steam heating coils. Here, the soap ages and various solid impurities, picked up in the processing equipment, settle out. The liquid remains in these tanks for an indefinite period, usually longer than a week, depending upon available indoor storage space. Hatches are provided at the tank bottoms through which settled sludge can be manually removed when necessary.

Aging of liquid soap has a definite effect upon quality. Certain metallic stearates which crystallize very slowly are allowed time to settle out. Also, small amounts of materials which are very difficult to saponify may not have reacted in the kettle. During the aging process, these materials do react, though very slowly, and a definite drop in alkalinity can be detected.

From the settling tanks the soap is centrifugally pumped to cooling tanks on the third floor of the manufacturing building. These tanks are equipped with cooling water coils, and the liquid temperature is lowered to about 60° F., to precipitate dissolved impurities before filtering. The soap goes from the cooling tanks into hand screw or hydraulically operated plate-and-frame filter presses utilizing heavy duck filter cloth. The largest of these presses contains 62 plates, each 36 inches square. The filtered product flows by gravity from the presses into liquid soap storage tanks from which it is removed for shipping. Total liquid soap storage capacity is about 44,400 gallons.

It is possible—for example with a rush order—to by-pass the outdoor settling tanks and pump directly from the kettle to the cooling tanks and filters. The end result is about the same, but the filtering operation becomes more difficult since impurities that would otherwise have settled out prior to filtration must be removed.

Glycerol, making up about 11% of the total solids in a finished 40% coconut oil–potash soap, exhibits a bodying action which makes the soap more viscous than some users prefer. The viscosity can be reduced by about one third by addition of potassium chloride to the extent of 0.5% of the total solids. The procedure is not injurious to the soap's appearance and improves its handling qualities. An equal amount of chelating agent has a similar effect (*7*).

Liquid scrub soaps, made by approximately the same method used for toilet soaps, do not as a rule require the clarity of the latter. They are not filtered, therefore, but go directly from kettle to storage and are ready for shipping.

Paste Soaps Contain 47% Solids

A typical paste soap formulation is:

	Pounds
Coconut oil (manila)	900
Potash (40° Bé.)	586
Water	1200
Perfume	5
Coloring matter	60 (grams)

This soap is made in kettle No. 3 (crutcher) of Table II. When finished it will contain about 47% solids (soap plus glycerol) and will have a free alkalinity of 0.15 to 0.25% as potassium hydroxide. Paste soaps, intermediate in firmness between liquid and bar soaps, are quite generally dissolved in water by the customer and employed as liquid soaps for scrub or toilet use.

About 250 pounds of water is first metered into the crutcher. This procedure, by lowering the initial concentration of reactants when the potash and coconut oil are started into the kettle, slows the beginning of saponification. If this is not done, significant amounts of unreacted oil and potash are trapped in portions of the charge which saponify inhomogeneously almost immediately upon mixing. Agitation time and the final concentration in the crutcher are such that the entrapped reactants are not freed for saponification, and a nonhomogeneous soap results. This method is not necessary with a liquid soap because the initial reactant concentrations are much lower.

After the initial water, potash (which has been diluted to 40° Bé.) and coconut oil are metered into the crutcher, agitation is begun, and the perfume and coloring matter are added. Agitation is continued until the charge begins to thicken, indicating that saponification is well under way. Steam is then introduced into the crutcher jacket. When the entire batch appears to be thick and homogeneous, open steam is turned on and agitation is continued for about 20 minutes. Temperature reaches a maximum of about 212° F. During this period, the soapmaker periodically dips out samples, allows them to gel, and tests alkalinity by dropping phenolphthalein on the sample. Alkalinity may also be checked by dropping phenolphthalein directly into the kettle as with the liquid soaps. When the alkalinity looks about right, the remainder of the water is added; hot water is used to reduce foaming. The clarity and consistency of the gelled samples tell the operator when the solids concentration is within limits. If water content is too high, the sample will be too thin, if too low, it will not be sufficiently clear. An experienced soapmaker can adjust concentrations within 1 or 2% using such tests.

When laboratory analyses show concentration and alkalinity to be satisfactory, the crutcher is stopped, steam is turned off, and the hot soap is dropped directly into drums or smaller containers, where it cools, gels, and is then ready for shipping. Time in the kettle for this soap is about 1 hour and 20 minutes from the time the crutcher is started.

Both Caustic and Potash Are Used to Make a 70% Shampoo Bar

The bar soap for which the formulation is shown is cold-made:

	Pounds
Coconut oil (cochin)	1340
Caustic (fortified 33° Bé.)	675
Potash (40° Bé.)	77
Water	38
Perfume	5
Antioxidant	2
Coloring matter	45 (grams)

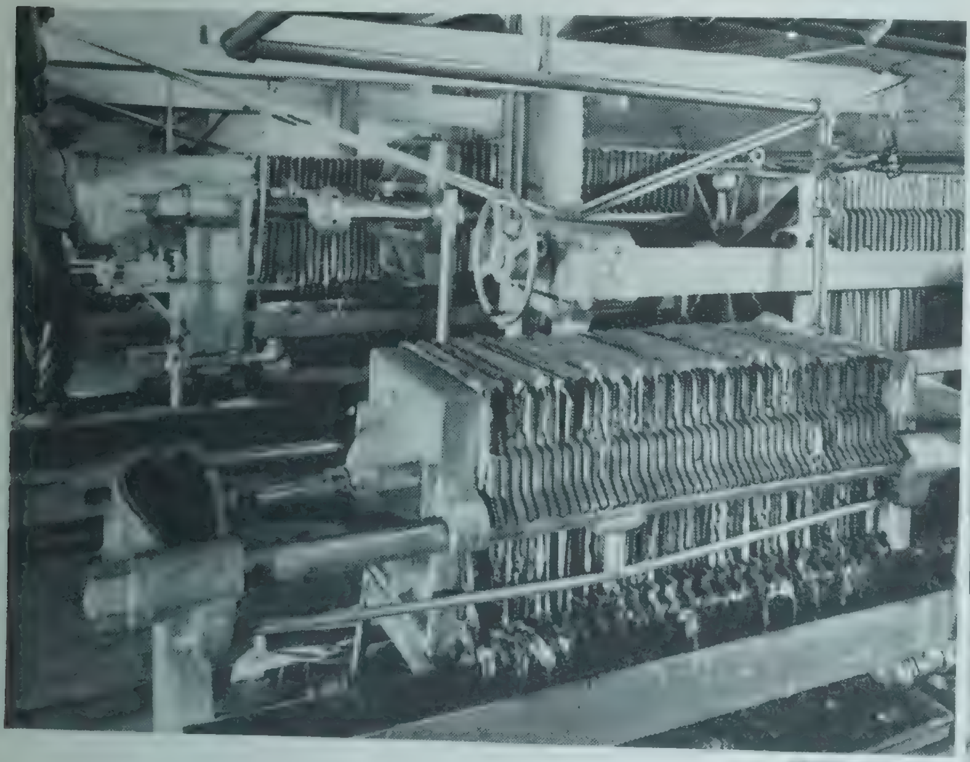
This soap is made in kettle No. 4 (crutcher) of Table II. Its final concentration is 70% solids (soap plus glycerol), and it has an acidity of 0.4 to 0.5% as oleic acid. It is used as a shampoo, principally in beauty shops.

The coconut oil is metered into the crutcher and heated to 90° F., using the steam jacket. The steam is then turned off, agitation is begun, and the caustic, potash, and water, which have been blended in a common tank, are charged by gravity. The latter ingredients are weighed, rather than metered, to ensure quantitative accuracy. The perfume, coloring matter, and antioxidant are then introduced. Agitation is continued for about $1^1/_4$ hours, until the batch is homogeneous and saponification is well under way. When the proper consistency has been obtained, as determined by the soapmaker's judgment, the batch, now at about 120° F., is pumped directly into frames on the second floor by means of a horizontal, simplex, steam-driven pump. The frames are open-topped, rectangular steel boxes, 48 × 16 × 42 inches, are dolly mounted, and hold about 2000 pounds of soap. Saponification continues in the frames, where 220° F. may be reached, until the reaction is completed.

After 1 to 2 days in the frames, a laboratory analysis is made; if it is satisfactory the solid slabs of soap are removed from the frames for cutting. The cutting machines are rectangular iron tables fitted at one side or one end with vertical frames in which taut, regularly spaced steel wires are strung. Slabs of soap are placed on the table and forced through the wire-strung frames. The soap cutters are adjustable—1-pound, 2-pound, and $3^1/_2$-pound bars are the usual sizes. Careful procedure holds the amount of scrap soap from the cutting operation to below 10%. Scrap is saved and recharged to the appropriate kettle. The cut bars are individually wrapped and packed in cartons for shipping.

Dry Cleaning Soaps Are Easy to Make, Difficult to Develop

Dry cleaning soaps constitute a large part of Davies-Young's business, and although their manufacture is fairly simple, the



▲ Liquid Toilet Soaps Are Filtered Before Storage or Shipment

Liquid Soap Runs from Storage Tanks into Shipping Drums ▶

development of effective formulations is not. The formulation given here, although no longer widely used, adequately demonstrates present industry practice in preparing these materials.

	Pounds
Oleic acid	2016
Stoddard solvent	2600
Xylene	800
Isopropyl alcohol	250
Potash (40° Bé.)	260
Flaked potash	134

Kettle No. 5 (crutcher) of Table II is used in this process. All the ingredients going into a dry-cleaning batch are accurately weighed. The oleic acid, Stoddard solvent, isopropyl alcohol, and xylene are first introduced into the kettle. The liquid potash is heated to 140° F. in a separate container, and the flake potash is stirred into it. Agitation is then begun and the enriched potash solution is charged to the crutcher. Reaction is complete about 30 minutes after addition of the potash. Reaction temperature is about 115° F. The batch is gravity fed directly into drums or smaller containers for shipping. The only laboratory work necessary for this soap is a solubility test in Stoddard solvent, the material with which it is generally mixed for use in dry-cleaning plants.

Production Control Is Important Laboratory Function

All laboratory methods used are based upon the methods of the American Oil Chemists' Society (*1*). Production control tests are the most frequently employed.

The solids content of a soap is determined by the Brabender oven test. A 5-gram sample is heated in the oven for 1 hour at 135° C. The amount of water present initially is represented by the loss in weight following heating.

To determine free alkalinity as potassium hydroxide, a 10-gram sample dissolved in $0.1N$ oleic acid is back titrated with $0.1N$ potassium hydroxide.

To determine free acidity as oleic acid, a 10-gram sample is dissolved in neutral denatured alcohol and is then titrated with $0.1N$ potassium hydroxide.

Corrosion Is Not Serious

Corrosion is not a serious problem in the Davies-Young operation. Oleic acid, the most corrosive material handled in large quantities, is stored in lead-lined tanks and pumped with a Duriron No. 50 noncorrosive centrifugal pump. With the exception of a few small stainless steel kettles for highly specialized materials, all other major equipment is low carbon steel.

A small amount of iron goes into solution in the soybean fatty acid storage tanks. The tanks are not seriously affected, but the fatty acids tend to become discolored, and filtration of liquid soaps of which they are a constituent is made more difficult. A brush-on plastic protective coating for the storage tank interiors is currently under investigation.

Polyethylene liners are used in certain paste soap shipping drums to prevent the entry of rust into the soap. These drums are not completely filled, and rust is likely to form on interior areas which are not covered with soap. The problem is not prevalent with liquid materials because they surge about in the drums and keep the interior surfaces fairly well covered with soap. Also, the slightly higher alkalinity of the liquid soaps seems to have some corrosion inhibiting effect.

Alert Research Is Key to Successful Future

To boost versatility and productive capacity, two additional 10,000-gallon tanks, adaptable to either storage or certain types of manufacture, are being installed at Davies-Young. Continuous soapmaking equipment is available, but its suitability for specialty soap manufacture is still a question. The time required to stabilize entering reactant streams in such equipment might be prohibitive for the relatively short production runs now used. Present manufacturing personnel, who are in essence craftsmen, would have to be replaced by technically trained people. The relatively small proportion of production cost now represented by labor and overhead is another important factor in any consideration of a shift to continuous equipment.

Chemical refining of fats and oils in the plant, currently under consideration, is largely a question of economics: Will the cost of such a process be overbalanced by the savings resulting from buying lower quality fats and oils?

The future of the specialty soaps producer, believes Davies-Young, lies in the ability to stay one step ahead of industrial needs. Basically, this means an alert developmental research program. In line with this philosophy, the company is making additional laboratory space available and is building a replica dry-cleaning plant for research in that field.

Customer service is becoming important with the return of higher sales resistance; a program offering essential laboratory services to users of the company's dry-cleaning formulations has been in operation for some time.

While synthetic detergents are becoming ever more popular and are supplanting soaps in many uses, there appear to be a substantial number of applications in which such materials cannot replace soap in the foreseeable future. The company has entered the synthetic detergent field, nevertheless, because consumer demands so require.

Keeping ahead of industrial cleaning and maintenance needs also has resulted in the company's entry into fields other than, but closely related to specialty soap manufacture. Floor waxes and sealers and polishing compounds are examples. Waxes for aircraft and automobiles and cosmetics are produced by subsidiary companies.

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Ammonia-Base Sulfite Pulping

WILLIAM Q. HULL, *Associate Editor*

in collaboration with

BEVERLY C. SMITH
Crown Zellerbach Corp., Lebanon, Ore.

JAMES H. HULL
Crown Zellerbach Corp., Camas, Wash.

WALTER F. HOLZER
Crown Zellerbach Corp., San Francisco, Calif.

EARLIER reports in this series described the romantic, centuries-old, history of pulp and papermaking. Two described kraft pulp production and kraft papermaking; a third portrayed comparatively new magnesia-base sulfite pulping (*7*, *14*, *15*). This article presents the ammonia-base pulping process, which is currently receiving more attention than any other in the field of introducing soluble base to normal sulfite pulping. Historical comment on processes not employing ammonia will not be repeated; too, most of the detailed description will be on unit operations and processes that are dissimilar to those of plants previously pictured in the staff-industry collaborative series.

In brief review, there are three principal processes for production of chemical wood pulp—soda, sulfite, and kraft (or sulfate). The order of production by the three processes is shown in statistics for 1953 (*17*) and in Table I.

	Thousand Tons
Soda	428
Sulfite	2321
Kraft	9435
Other chemical	677
Nonchemical and semichemical	4664

The three chemical processes are all concerned with methods for removing the lignin, which binds the cellulose fibers in wood, and retaining the fibers with a minimum of degradation. Typically in the soda process, a 12.5% solution of sodium hydroxide and sodium carbonate in approximate ratio of 85:15 is used as a cooking liquor to dissolve noncellulosic materials from the wood; sodium hydroxide is responsible for the dissolving action. The kraft or sulfate process employs a mixture of sodium hydroxide and sodium sulfide. The sulfite process achieves the same results with an acid cooking liquor. In the long-used calcium bisulfite process, the cooking liquor composition is 7% by weight sulfur dioxide of which 4.5% is combined as sulfurous acid and 2.5% as calcium bisulfite (*16*). In magnesia-base sulfite pulping, magnesium oxide is substituted for limestone, and the resulting cooking liquor consists of magnesium bisulfite in an excess of sulfur dioxide.

Compared with calcium-base pulping . . .

AMMONIA PULPING has

Many advantages

- . . .less sulfur per ton required
- . . .decrease in cooking time
- . . .less steam per ton
- . . .less maintenance on digesters and pumps
- . . .reduction in cost of handling and storing ammonia as compared with dolomite or lime rock
- . . .more uniform acid making
- . . .spent liquor not burned can be spray-dried and converted to salable by-products
- . . .significant increase in physical strength and viscosity
- . . .for paper, superior quality and uniformity

Few disadvantages

- . . .slime growth in knotters to deckers system. Controlled by use of organomercurial slimicides
- . . .redder pulp with western hemlock, but requires no additional chlorine for bleaching (however, if combine is kept as high as on calcium base, pulp would be just as bright.)
- . . .more expensive linings on digesters and pumps

Decrease in sulfur is attributed to decreased combined sulfur dioxide (from 1.30% to 0.85%) with no sacrifice in pulp properties except unbleached color. The faster cook cycle is due to quicker and more uniform penetration of chips by bisulfite cooking liquor and to the decreased combined sulfur dioxide below levels possible with calcium.

New processes for pulp making have been sparked by problems of disposal of the spent cooking liquor and soluble components of wood as much as by the desirability of changes in the characteristics of the end product. The cellulose content of various woods in the United States ranges from 51 to 65% (*11*); this is the primary constituent of the pulp product. It is seen, therefore, that approximately half the wood entering a pulp mill is dissolved by the cooking liquor. In the sulfite process there is approximately 2000 gallons of spent liquor (12% solids) for each ton of pulp produced. In the standard calcium-base process, the solids consist of lignosulfonic acid (65%), reducing sugars (20%), sugar–sulfur dioxide derivatives (8.4%), and calcium (6.7%).

It is the disposal of huge volumes of spent liquor and its contained organic matter (estimated to be 4,900,000 tons yearly) that has been one of the major problems of the pulp industry. In earlier days, unrestricted discharge into streams was practiced; however, inasmuch as some of the sugars and organic acids become consumers of oxygen, the dissolved oxygen became depleted. In the past two decades, disposition of the liquor by other means has been investigated as a result of concentrated industrial and legal efforts toward stream improvement.

Many of the early efforts were in the direction of reducing the biological oxygen demand of the waste liquor making it suitable for stream discharge. Trickling filters, reaeration, and chemical alteration of the carbohydrate portion of the liquor were investigated. All added considerably to the cost of pulp making and none recovered the carbohydrate portion of the spent liquor. Others have converted the organic matter into useful compounds, including alcohol, yeast, vanillin, oxalic acid, tanning material, road binders, special cements, cement accelerators, and plastics. Such efforts have ranged from failure to commercial production. Production of food yeast from sulfite liquor as practiced in the plant of Lake States Yeast Corp., Rhinelander, Wis., was described earlier in this series (*9*).

Second only to the problem of spent liquor disposal is consideration of the heat value of the dry organic solids in the spent liquor and recovery of cooking chemicals. The heat content ranges from 7000 to 8000 B.t.u. per pound. Many processes have been investigated for evaporating the calcium-base liquor and using the concentrated liquor as fuel. The concentrated liquor can satisfactorily be used under proper conditions for generation of steam.

However, inasmuch as the calcium and the sulfur combine during the burning operation to form calcium sulfate, from which the cooking compounds cannot be recovered practically, the processes have not been particularly attractive. Sodium has been substituted for calcium as a pulping base and is used in a limited number of mills. However, the recovery of the base as usable chemicals for the sulfite pulping process is complicated and costly.

Substitution of magnesium for calcium has been extensively investigated. In this process, magnesium is recovered in the form of magnesium oxide and is suitable for re-use as such. A history of the process and its commercial application in the 275-ton-per-day plant of Weyerhaeuser Timber Co. at Longview, Wash. (the only commercial magnesium oxide plant until recently) were related in this series (*7*). This plant converted to magnesia-base pulping following satisfactory pilot plant operation beginning in 1940. Over-all operation and recovery have been satisfactory, and the system offers a definite method of stream improvement. Magnesium consumption is approximately 50 pounds per ton of pulp produced; sulfur consumption is 85 pounds per ton of pulp. With sufficient evaporator capacity, both these figures would be expected to be somewhat lower. They compare, nevertheless, with a consumption of approximately 270 pounds of sulfur and 350 pounds of lime rock for the conventional calcium-base pulping. A second magnesium-base plant has just begun operation at Ketchikan, Alaska. Owned by Ketchikan Pulp Co. (a combine between American Viscose Co. and Puget Sound Pulp and Timber Co.), the new plant, built at a cost of approximately $52,500,000, produces 350 tons of dissolving pulp daily. The magnesium oxide recovery system is probably more adequate, and it is expected that chemical consumption figures will be materially better than those experienced at the only prior mill using the process.

Magnesia-base pulping has several advantages: stream pollution is avoided; cooking chemicals can, in large measure, be recovered; and energy requirements of a mill can be supplied through the burning of the organic solids in the waste liquor. Yeast or alcohol can also be produced by running the partially concentrated liquor through an alcohol plant and returning the still slop to the recovery system.

A single, important disadvantage, however, is extremely high initial cost or cost of conversion. For this reason, in existing mills the substitution of ammonia for conventional calcium is considered by many to be a more practical solution. However, any new sulfite mill will undoubtedly analyze the two processes thoroughly before deciding which it will use. This is particularly important because of the greatly increased production of ammonia during and since World War II.

With the recent and current interest that has been shown in the substitution of ammonia for calcium in the conventional sulfite process for making pulp, it would be reasonable to assume that the modified process is a new development. However, experimentally and commercially, the process has been known for many years. A patent was issued to Braun in Germany in

Table I. U. S. Wood Pulp Production (*17*)

(Thousands of short tons)

	Dissolving and Special Alpha	Sulfite Paper Grades		Sulfate Paper Grades									
		Bleached	Unbleached	Bleached	Semibleached	Unbleached	Soda	Total Chemical	Groundwood	Defibrated, Other Nonchemical	Semichemical	Semi-Screenings	Total All Grades
1937	354	995	792	215		1924	508	4,787	1601		133	53	6,573
1938	228	776	602	321		2123	395	4,445	1333		119	37	5,934
1939	193	1024	729	424		2538	442	5,351	1445		152	46	6,993
1940	327	1285[a]	996	453	131	3163	532	6,888	1633	210	165[a]	64[a]	8,960
1941	262	1442[a]	1216	659	164	3704	480	7,925	1886	267	200[a]	97[a]	10,375
1942	404	1313[a]	1213	653	159	3927	462	8,131	1870	406	210[a]	167[a]	10,783
1943	390	1163[a]	883	602	147	3487	419	7,092	1767	495	231[a]	96[a]	9,680
1944	447	1076[a]	863	665	144	3740	413	7,348	1769	532	285[a]	175[a]	10,108
1945	383	1161[a]	816	705	149	3618	430	7,261	1827	560	295[a]	224[a]	10,167
1946	317	1376	784	750	152	3686	476	7,541	1951	616	320[a]	178[a]	10,607
1947	407	1495	894	909	193	4255	492	8,644	2050	693	444	114	11,946
1948	420	1490	902	1040	225	4749	510	9,335	2175	745	478	140	12,872
1949	374	1455	707	1118	264	4595	492	9,006	1960	604	506	131	12,207
1950	479	1629	741	1433	360	5709	522	10,872	2216	935	686	140	14,849
1951	616	1761	765	1900	294	6379	446	12,160	2474	945	797	150	16,524
1952	706	1692	673	2083	275	6211	425	12,065	2380	1059	829	140	16,473
1953	677	1767	594	2379	303	6753	428	12,861	2379	1116	1029	141	17,525

[a] Estd. from U. S. Bureau of Census combined data.

1902 covering an early version of ammonia pulping. As we know it today, the process was patented in England in 1923, Germany and France in 1924, and in the United States in 1925. The American patent (*3*) describes the system as:

> A sulfurous acid process for resolving wood substance, which process consists in heating the wood substance with an aqueous sulfurous acid solution to which has been added a calculated small amount of ammonia.

The first company to use the process commercially was Norsk Hydro-Eletstrisk Kvaelsofaktieselskab, a large Norwegian ammonia manufacturer, in its mill in Toten, Norway, in 1936. Reported advantages of ammonia pulping as contrasted with ordinary calcium sulfite pulping at the time of conversion of this plant were a reduced cooking time at a lower temperature, a higher yield of cellulose per unit of wood, and a cellulose low in ash (*8*). The plant has used the process continuously since that time.

In the United States, ammonia-base pulping was pioneered commercially by Rayonier, Inc., whose plant at Shelton, Wash., was converted from calcium pulping in 1945. The plant has a capacity of 300 tons per day. Eastern Corp. followed with conversion of two plants in Maine in 1947 and 1948. The Lebanon mill of Crown Zellerbach, subject of this article, began in 1949. Wausau Paper Mills became the first midwestern mill to change over to ammonia cooking in 1950. Rayonier's second plant to convert, located at Hoquiam, Wash., produces 400 tons per day which is the largest ammonia-base production at any one plant.

The National Production Authority, U. S. Department of Commerce, surveyed American pulp mills in 1953 to determine the status of ammonia pulping. The study revealed the following information:

No. mills surveyed	62
No. returns	62
No. mills using ammonia process	10
No. anticipating use in next 3 years	9

	Annual Pulp Capacity, Tons	Estimated Annual Ammonia Consumption, Tons
62 mills	3,064,000	...
10 mills now using	505,000	26,250
9 mills probable	338,000	18,050

Table II. North American Mills Using Ammonia-Base Pulping (*10*)

Company	Location	Production Tons Pulp/Day	Date of Conversion
	United States		
Rayonier, Inc.	Shelton, Wash.	300	1945
Eastern Corp.	S. Brewer, Me.	155	1947
Eastern Corp.	Lincoln, Me.	90	1948
Crown Zellerbach Corp.	Lebanon, Ore.	55	1949
Wausau Paper Co.	Brokaw, Wis.	90	1950
Consolidated Water Power & Paper Co.	Wisconsin Rapids, Wis.	140	1951
Rayonier, Inc.	Hoquiam, Wash.	400	1952
Columbia River Mills[a]	Vancouver, Wash.	110	1952
Scott Paper Co.	Anacortes, Wash.	100	1952
St. Regis Paper Co.[b]	Bucksport, Me.	100	1953
Scott Paper Co.[c]	Everett, Wash.	310	1954
	Canada		
Fraser Co., Ltd.[d]	Edmundston, N. B.	350	1953
Restigouche Co., Ltd.[e]	Campbelltown, N. B.	260	1954
Irving Pulp & Paper[f]	Saint John, N. B.	150	1954
Canadian International Paper Co.	Gatineau, Que.	180	1954

[a] Currently considering converting plant at Salem, Ore., to ammonia pulping.
[b] Currently running comparative tests.
[c] Converting in August 1954
[d] Converted on trial basis November 1953; currently continuing on trial basis.
[e] Converted on trial basis June 1954; currently continuing on trial basis.
[f] Extended trial scheduled to start September 1954.

The U. S. and Canadian mills actually using ammonia pulping at this time are shown in Table II (*10*).

Ammonia-base pulping, basically, is identical chemically with calcium pulping except that the ammonium ion is substituted for the calcium ion in the bisulfite cooking liquor. There are several advantages, however, over other modified sulfite processes. An important one is that the change-over is relatively simple and requires little modification of existing equipment. Because ammonia-base liquors do not have the scaling properties of calcium-base liquors, they are not adequately retained by linings used for calcium-base plants. These linings, however, can be replaced after conversion, as necessary in the regular maintenance program.

Principal additions to the plant are the storage and handling facilities for ammonia. The spent liquor can be burned satisfactorily, and stream pollution is eliminated. In addition, at least partial recovery of cooking chemicals is possible. A favorable consideration is possible utilization of some woods, such as jackpine, maple, beech, and others, normally difficult to pulp, as result of a better penetration rate and more favorable side reactions in ammonia pulping. (The mechanisms of chemical side reactions are not completely understood. This much seems certain, though perhaps oversimplified: Products of side reactions due to chemicals in the wood together with ammonia salts are soluble whereas similar calcium products are not. Removal of the calcium base from the reaction by precipitation very seriously alters the course of the main reaction.)

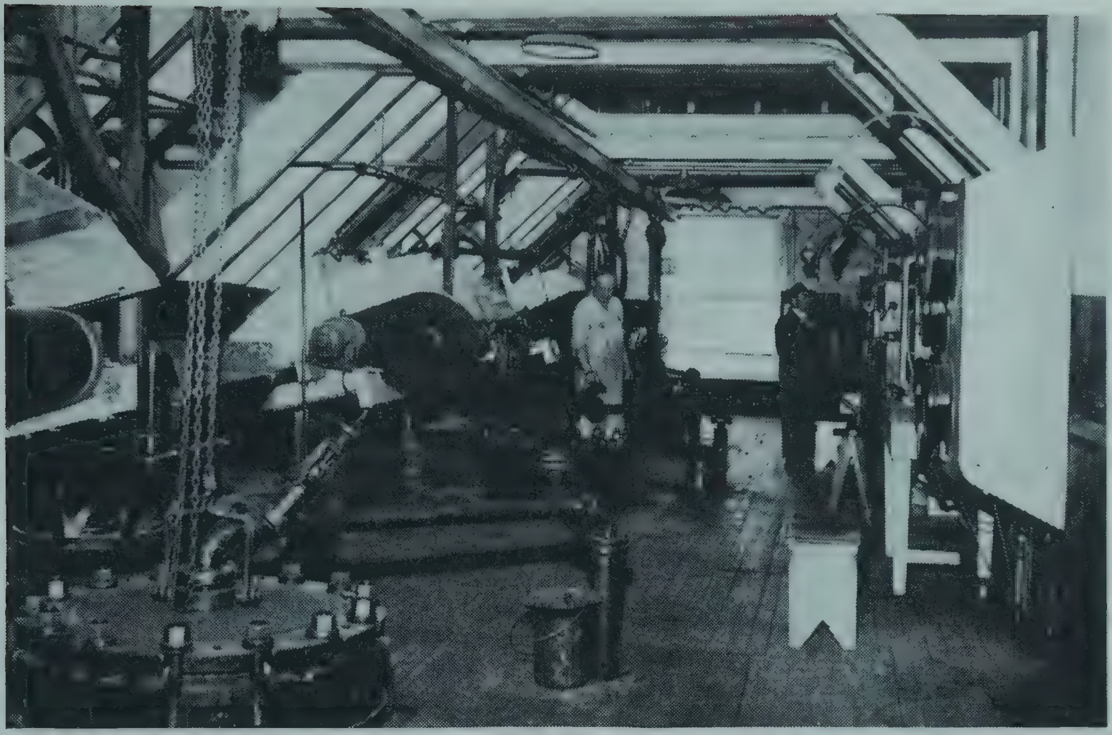
Future conversion to ammonia pulping represents a sizable market for ammonia, and ammonia producers have cooperated closely with pulp mills in problems accompanying a change from calcium-base pulping. Nitrogen Division, Allied Chemical and Dye Corp., has actively participated in the conversion of most of the mills other than Rayonier's, and Allied's observations of the process in a number of conversions have been published (*5*).

Ammonia Pulping Is Practiced at Lebanon, Ore., Plant of Crown Zellerbach Corp.

This plant was converted in December 1949 as a joint venture by Crown Zellerbach and Soundview Pulp Co. The two companies constructed a pilot plant in 1951 to study evaporation and burning of the liquor and sulfur recovery. The pilot plant and its operation have been summarized (*6*). In 1953, Crown Zellerbach installed an evaporation, burning, and sulfur recovery system at the plant.

Crown Zellerbach Corp. operates pulp and paper mills in West Linn, Lebanon, and St. Helens, Ore., Port Townsend, Port Angeles, and Camas, Wash., Ocean Falls and Elk Falls, B. C., and Carthage, N. Y. Both kraft and sulfite processes are employed. The plant at Lebanon is one of the company's smallest and oldest operations. First known as O'Neil and Callaghan's mill, the plant was constructed from an old flour mill and produced its first pulp and paper products in 1890 (*18*).

Of historical interest is the fact that until 1906, straw was used in papermaking in this plant. Waste straw was purchased from farmers for $3.50 to $4.00 a ton, and during that period, huge stacks of loose straw (often several blocks long and 50 to 60 feet wide) piled high, dominated the Lebanon landscape. First product from the mill was butcher wrapping paper. In a more



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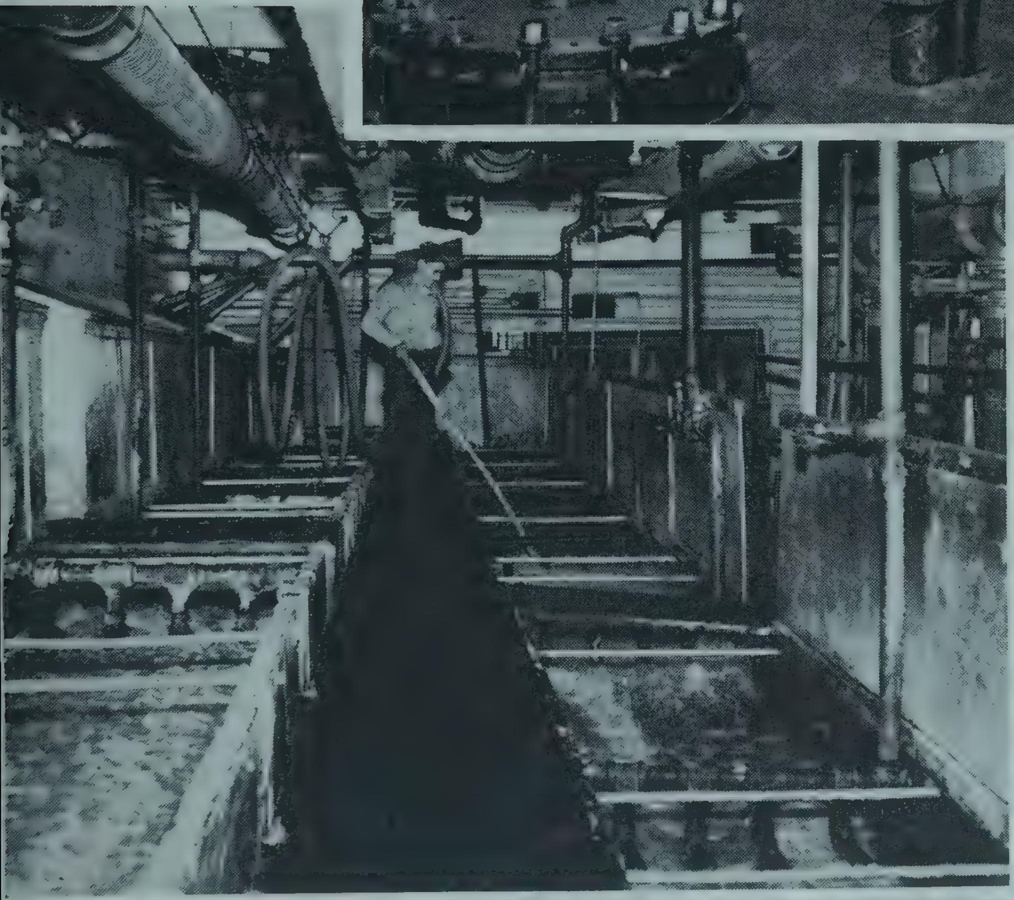
Chips are charged from overhead storage bins to one of three digesters; on charging floor, only tops of units, 40 feet high, are visible; charging hopper is at left

Ammonia-Base Pulping



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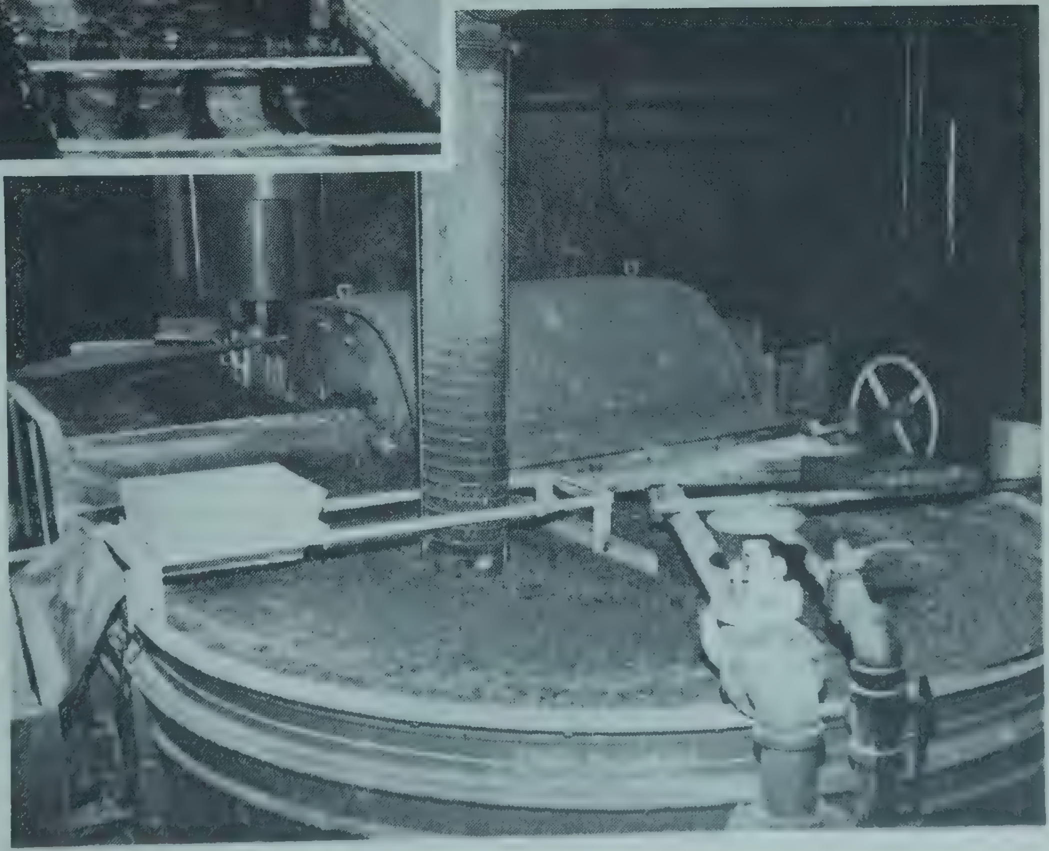
Typical flat screens, which depend for their operation on a combination of gravity flow and suction from diaphragms, are used to remove fine knots, fiber bundles, and dirt after the pulp has been coarse screened



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Size, alum, and dyes are added to pulp in a Hollander-type beater; at Lebanon very little hydration occurs in the beater, which is usual in other plants esthetic vein, the pioneer papermakers were proud that some of their fine wallpapers, made from straw, found use in the White House in Washington.

The O'Neil-Callaghan mill became Lebanon Paper Co. and was subsequently purchased by Crown Zellerbach Corp. The plant has a rated capacity of 60 tons per day. Chief products include a special cartridge wrap for the explosives industry and butcher and merchandise wrap. The plant does not produce bleached products. Much of the plant's producing machinery and equipment has been in service many years, and numerous modifications have been made, some very basic. Those that have undergone major changes over the years are not listed in the usual manner in the Processing Equipment bibliography.

The mill is located on the south fork of the Santiam River in the Willamette Valley (approximately 85 miles south of Portland). Hemlock (90%) and white fir (10%) represent chief woods used. These are bought on the open market on a grade and board foot basis. The mill issues purchase orders to its suppliers in the spring so that each can anticipate his volume of wood to be delivered to the mill. Logs are brought to the mill by trucks from growing areas within a 70-mile radius. In earlier years, logs were received on a year-round basis. Within the past few years, however, use of wood chips from saw mill wastes has grown to 25 to 30% of the plant's wood raw material, resulting in a corresponding decrease in use of logs. Deliveries are now chiefly restricted to the period from summer to late November. The chips may be used alone or blended with those from purchased logs.

Upon arrival at the mill, logs are inspected and graded. This is done by independent log graders who class logs in decreasing order of quality as Grade 1, 2, or 3 on basis of many factors (number of knots, rot, soundness, etc.) as specified in applicable grading rules (*2*). Graded logs are lifted from trucks by an unloading crane which handles 35 loads per 12-hour day during the heavy summer and fall seasons. Logs are bundled by loads and tied with No. 6 baling wire, inventoried, and towed by motor boat to the desired area of an 8- to 10-acre artificial storage pond. Each bundle or truck load contains approximately 5000 board feet, log scale (equivalent to slightly over 10 cords of wood). About 5,000,000 feet (log scale) can be stored in the pond.

It is desirable to turn over the entire pond contents each year, but it is a "must" to do so every other year. "Cold-deck" storage is provided on the banks surrounding the pond. A heel boom crane mounted on a flat-bed railroad car lifts logs from the pond and stacks them for this additional storage which, in 1953, provided 7,000,000-foot capacity.

In the wood mill, logs from the storage pond are sawed, barked, and split and then conveyed to the chipper for size reduction. From the storage pond, the logs are floated in bundles to the log haul-up, which takes the individual logs up an incline to the mill. Individual logs that have too high a water content, commonly called "sinkers," are identified as such so that when the logs are temporarily returned to the storage pond after sawing, sinkers will be routed directly to the mill for processing and not allowed to sink to the bottom of the pond.

The cutoff saw has a 72-inch diameter blade and is operated at 487 r.p.m. by a 50-hp. motor. It serves a double purpose: logs up to 48 inches in diameter are cut to 8- to 12-foot lengths for the barker; and after barking, the logs are cut by the same saw to 4- or 5-foot lengths.

Wood bark has little or no pulp value. It also is highly colored and contains dirt and other extraneous matter. All must be removed before the conversion to high quality pulp. Older methods of barking were by friction through tumbling or rotating the logs in a drum or in a stationary machine with agitating cam equipment. Hydraulic barkers are more common today. The hydraulic barker at Lebanon was converted from an old plane barker. A traveling arm moves at 1-foot-per-second lengthwise of the logs. Water, at 1250 to 1350 pounds per square inch, is directed on the log by jets ($^5/_8 \times {}^3/_{16}$ inch nozzles) mounted on the traveling arm. These jets reciprocate in a direction at right angles to the logs. After getting a pass down its length, the log is rotated 90°, and the arm travels back in the opposite direction and barks a second quadrant of the log. In two full trips, the barker generally removes all of the bark present. The barker uses approximately 200 gallons of water per minute; it takes 1 minute to bark a 12-foot log. The machine is generally operated for two shifts a day.

The problem of bark disposal must be considered by every pulp mill. Depending on the type of wood, success in utilization has varied. Bark from southern pine has been used in making roofing felt. Spruce bark has been used in the manufacture of board and cheap grades of wrapping paper. Insulating materials have been made from finely shredded balsam fir and spruce barks. Potentially, some barks are a source of wax.

The most common disposal is as fuel. The heating value of moist bark (based on dry bark heating value of 8500 B.t.u. per pound) ranges from an effective B.t.u. content of 7250 (to 5580 with a range in water content of 50 to 70%) (*12*).

At Lebanon, bark is routed to the hog fuel pile (saw mill waste) for burning. The plant uses approximately 120 units of 200 cubic feet each of hog fuel daily.

From the hydraulic barker, logs are conveyed to the saw previously described, cut into 4- or 5-foot lengths, and then split into four or more pieces. A horizontal, steam-driven (125 pounds per square inch steam) splitter is used. The wedge-shaped, free-floating, steel cutting blade, 8 inches thick and weighing 200 pounds, is driven partially into the horizontal log in the 48-inch stroke of the piston, splitting the log into halves. Logs are turned by "jiggling" on the reversible flat conveyor chain and by holding with the splitter head, and the halves are split into quarters. On logs of large diameter, it may be desirable to repeat the operation. The splitter has a capacity of 50,000 feet in an 8-hour shift.

Some of the wood pieces contain areas of bark not removed by the hydraulic barker. This is usually around knots or other uneven areas. A hand-operated cleanup barker is used to remove such bark when present. It consists of a 30-inch revolving disk containing four knives. The disk rotates at 567 r.p.m. as the operator holds the block against it, and the bark is shaved off as the operator revolves the block.

The clean, barked wood is loaded by hand into flat cars on a narrow-gage track and towed to the chipping machine in the main mill building.

Chipping Department Reduces Wood to Small Pieces

In order that the cooking liquor may penetrate the wood quickly, completely, and uniformly, it is necessary that pieces from the wood mill be reduced to chips averaging $^5/_8$ to $^3/_4$ inch long and $^1/_8$ inch thick. Multiknife machines, containing from 3 to 12 knives, are generally used. The Lebanon chipper consists of a cast steel disk 84 inches in diameter, which is rotated at 600 r.p.m. by a 100-hp. synchronous motor (*16E*). The disk contains three hard carbon-steel knives 22 inches long. A 17 × 17 inch feed spout is inclined at an angle of 57° to the rotating disk and knives. An operator uses a sharp hook or pickaroon to pull a piece of the wood from the flat car and drop it into an inclined chute that feeds into the chipper spout. The wood is chipped as it comes in contact with the rotating knives. The chips pass through slots behind the disk knives into a pit below. The chipper has a capacity of 10,000 board feet per hour. On Pacific Coast woods, the knives must be sharpened after 4 to 6 hours of use.

Generally, wood from chippers contains from 1.5 to 5% sawdust and pin chips and 1.5 to 3% slivers. Chip screens are used to separate the good chips from the under- and oversized particles. In some plants, circular and shake type screens are used.

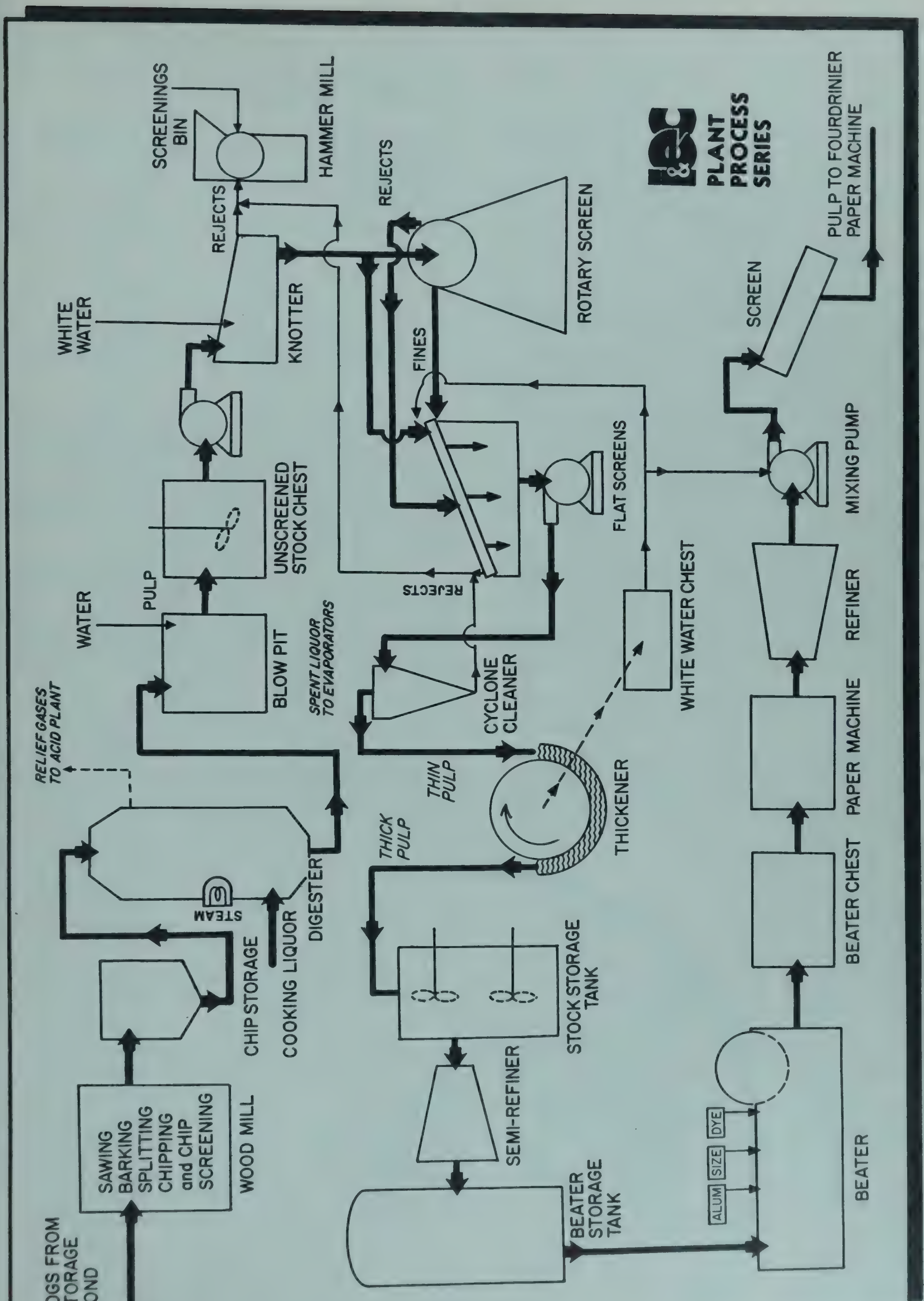

LOGS FROM STORAGE POND
SAWING
BARKING
SPLITTING
CHIPPING
and CHIP SCREENING
WOOD MILL
CHIP STORAGE
COOKING LIQUOR
STEAM
DIGESTER
RELIEF GASES TO ACID PLANT
WATER
PULP
BLOW PIT
UNSCREENED STOCK CHEST
WHITE WATER
KNOTTER
REJECTS
SCREENINGS BIN
HAMMER MILL
REJECTS
ROTARY SCREEN
FINES
REJECTS
FLAT SCREENS
SPENT LIQUOR TO EVAPORATORS
CYCLONE CLEANER
THIN PULP
THICKENER
WHITE WATER CHEST
THICK PULP
STOCK STORAGE TANK
SEMI-REFINER
BEATER STORAGE TANK
ALUM
SIZE
DYE
BEATER
BEATER CHEST
PAPER MACHINE
REFINER
MIXING PUMP
SCREEN
PULP TO FOURDRINIER PAPER MACHINE
I&EC PLANT PROCESS SERIES

Figure 1. Flow Sheet for Cooking, Screening, and Preparation of Pulp, Lebanon, Ore., Plant, Crown Zellerbach Corp.

Crown Zellerbach uses a double-deck vibrating screen (*18E*). The upper screen contains $1^{3}/_{8}$-inch holes on $2^{13}/_{16}$-inch centers, and the lower $^{1}/_{4}$-inch holes on $^{3}/_{8}$-inch centers. Fines (1 to 2% at this plant) are routed to the boiler room; slivers, which vary widely in quantity, are recirculated to the chipper.

Wood chips purchased from saw mills are dropped from railroad cars (holding 17 to 20 units) to conveyors which discharge to the chip screens. These are subsequently processed the same as those produced at the plant.

Chips of proper size are conveyed to chip storage bins which are located above the digester charging floor.

Crown Zellerbach Uses 10-Ton Digesters at Lebanon

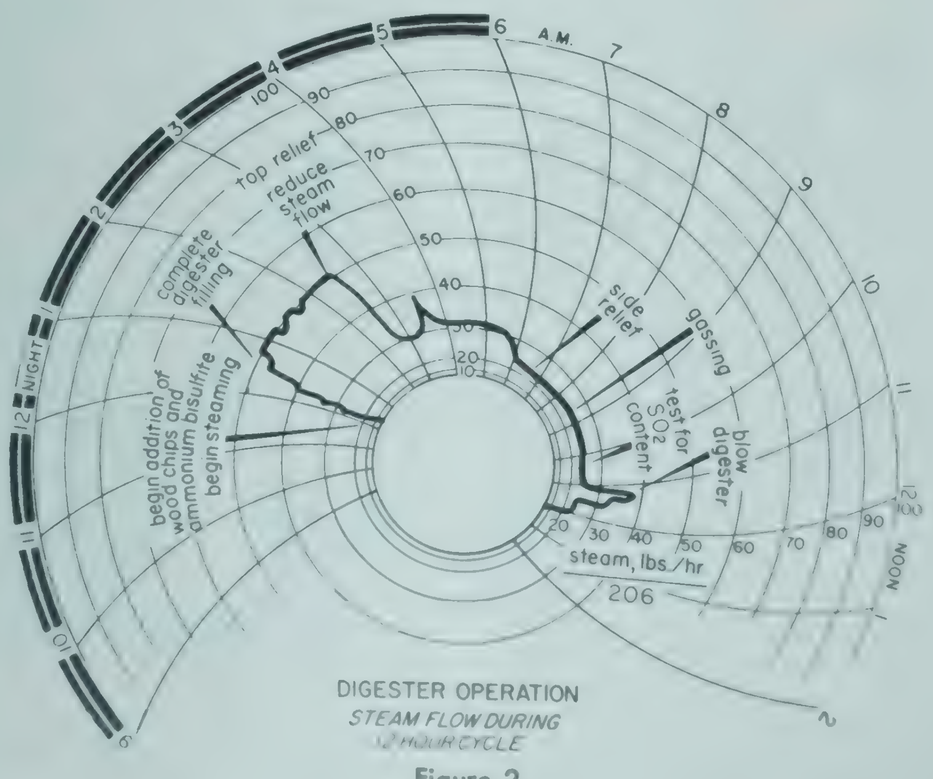
In production of pulp (Figure 1), the lignin and other undesired components of the wood are separated from the cellulose fibers in the cooking process.

Digesters in the industry are sized from a minimum of 10 tons to nearly 30 tons capacity. At Lebanon, Crown Zellerbach has three stationary digesters. They are 40 feet in over-all height, approximately 15 feet in diameter, and capacities range from 3700 to 4275 cubic feet. Each is fitted with a bell top and coned bottom. In the top is the charging opening; in the bottom, the discharge valve. The cylindrical center section is constructed of $1^{1}/_{8}$-inch steel plate. Each digester has an external, stainless steel (Type 316) heater (steam on outside) containing 108 tubes $1^{1}/_{8}$ inches in diameter and 12 feet long (300 square feet of heating surface). Linings before conversion from calcium bisulfite pulping were of standard acidproof brick with litharge-glycerol joints. These linings were replaced as needed with others especially designed for ammonia bisulfite liquor. Special features of the new linings are double-course, high density, acid-resisting brick with furfural-phenol jointing and with a membrane of the same material between the two courses. These have proved satisfactory.

Cooking cycles vary from 6 to 12 hours. In a typical 12-hour cycle currently used at Lebanon the procedure is as follows:

Chips (18 cords of wood, which makes 9 tons of pulp) are fed from the overhead bins by gravity through the charging hopper into the digester. Flow and packing of chips is aided by steam jets on the charging hopper. Ammonium bisulfite cooking liquor (Figure 3), containing an excess of sulfurous acid (preparation of which will be subsequently described) is added at the same time from the bottom. Cooking acid temperature is 86° F.; it contains a total of 6.50% sulfur dioxide (0.94% combined, 5.56% free). Approximately 21,000 gallons of the liquor is required to cover the chips. Filling the digester requires about 30 minutes. The lid is then secured. Two systems of steam are provided. During the first 8 hours, indirect steam (10 to 30 pounds per square inch in the heater) is used. For balance of the cooking period, direct steam is admitted ($3^{1}/_{2}$ hours).

Cooking liquor is circulated from the bottom of the cylindrical section to top and bottom of the digester through the heater by a centrifugal pump. As the cooking cycle progresses, pressure builds up because of sulfur dioxide from the cooking liquor as well as the presence of air in the chips. When it reaches 80 to 85 pounds, pressure is released through the top of the digester. Later in the process, pressure is "side relieved," gases and liquor being used to fortify the cooking liquor (Figure 2). Temperature reaches a maximum of 275° F.



DIGESTER OPERATION

STEAM FLOW DURING 12 HOUR CYCLE

Figure 2

After the digester is closed and cooking begins, time-temperature-pressure charts from a typical cook show the following data:

Time, Hours	Temp., ° F.	Pressure, Lb./Sq. Inch
0	86	0
1	100	31
$1^{1}/_{2}$	120	42
2	150	62
$2^{1}/_{2}$	180	85 (top relief)
3	187	85
$3^{1}/_{2}$	194	85
4	205	85
$4^{1}/_{2}$	207	85
5	211	85
$5^{1}/_{2}$	222	85
6	229	85
7	244	78 (side relief)
8	267	71
9	272	40
10	269	29
11	262	..

Toward the end of the cooking cycle, sulfur dioxide of the cooking liquor is determined by standard $NaOH-KIO_3$ titration (Palmrose method). Desirable final sulfur dioxide content is 0.4%. Samples are also compared with a set of color standards; when desirable color is reached, indicating completeness of cook, pressure is reduced to 30 pounds per square inch. The digester is blown at this pressure to a blow pit below.

There are three wood blow pits, each of which holds about 12 tons. Contents of the digester are discharged into the pits through 12-inch blow lines. Wood "target" blocks are mounted on the side of the tank opposite the blow lines, and the digester contents are directed toward the targets to break up pulp masses. Usually, 2 feet of 10% spent liquor (7000 gallons) is added to the blow pit before blowing to cushion the pulp.

Operation of the digesters or cooking process is favorable when compared with calcium bisulfite cooking. Good pulp is produced in cycles as short as 6 hours. It is very difficult to produce other than inferior pulp in 6 hours by calcium base. Generally the minimum time for calcium base would be about 7 hours. Longer cooking cycles are generally practiced when operations permit. A 12-hour cycle, as described above, is unusually long for U. S. practice. When lower temperatures can be used, effect on pulp is less drastic, and a better yield of stronger pulp is obtained. The pulp is also brighter and more easily bleached. At the same acid composition, rate of cooking in ammonia base is slightly more rapid than with calcium base. With ammonia base, however, combined sulfur dioxide can be lowered drastically without deteriorating the quality of the pulp. At lower combined sulfur dioxide, the rate of the cooking reaction is considerably increased and the cooking time or temperature can be lessened accordingly. (In test runs, cooking temperature has been reduced from 286° to 266° F. without changing the time of cooking.)

As mentioned, liquor color (along with chemical analysis) is a guide for blowing the digester. On change-over to ammonia pulping, it was necessary to establish a new set of standards as the liquor is considerably darker for any degree of cooking or delignification. Operators have found that color of the ammonia-base acid is a more reliable indication of degree of cook than it was when the calcium base was used. Generally speaking, the cooking procedure has proved more flexible and the pulp less subject to damage from improper treatment than they were before conversion.

Ammonia-Base Pulp Screens Easily

The digester charge which has been discharged to the blow pit consists of the insoluble, cellulose fibers together with the spent liquor containing all the soluble wood constituents. These must be separated before the pulp can be further processed. Rich liquor (containing 10 to 11% solids) is drained through a perforated stainless steel (Type 316) drain in the bottom of the blow pit to an outside storage sump. The blow pit is then washed, first with weak wash liquor and finally with water.

At a predetermined temperature (131° to 140° F.), which corresponds to a solids content of 9 to 10%, an air valve is automatically thrown, and the wash liquor is transferred to a weak liquor storage tank. At a second predetermined temperature (110° to 120° F.), which corresponds to a solids content of 1 to 2%, a valve transfers the weak washes to a sewer. All washes discharged to the sewer pass over a flume where samples are taken. Dissolved oxygen in the river is not allowed to fall below 5 p.p.m. (The disposition of spent liquors is described in the section of this report dealing with evaporation and recovery.)

In a larger or more complete installation for spent liquor recovery from the pulp, it is probable that rotary vacuum washes would be used.

It is important to remove as much of the cooking liquor as possible. Usually three washes are made, requiring $3^{1}/_{2}$ hours. The pH of final wash liquors is maintained at a minimum of 6 by addition of water. Lower pH's cause foaming.

The washed pulp is sluiced by gravity and addition of water to the unscreened pulp chest. This is an impeller-agitated concrete tank (capacity of 4800 cubic feet) divided into two channels by a (mid-feather) or central wall. From here it goes to the feed-box ahead of the knotter. The consistency is maintained at 3 to $3^{1}/_{2}$% through addition of water (*5E*).

One of the most important operations in the treatment of pulp is separation of uncooked slivers and knots from the cooked fibers and removal of dirt and other foreign matter. Various types of screens are used for these purposes; generally, the operations are divided into coarse and fine screening. In all, water plays an important role, providing both a medium for screening as well as a method of conveyance between screens. After screening, water, commonly called "white" water, is extracted and re-used. At Lebanon, knots and oversized particles are removed by a vibrating screen containing $^{1}/_{8} \times {}^{3}/_{4}$ inch slotted openings (*1E*). Tailings are passed to a hammer mill revolving at 1800 r.p.m., and discharge is used in certain coarse grades of paper (*9E*). White water is added at the knotter, reducing consistency of the pulp to 0.2 to 0.25% in order that fine screening can be accomplished.

Typical pulp mill flat and rotary screens are used for removal of small knots, fiber bundles, and dirt; final cleaning is by cyclone-type cleaners. Flat screens consist of bronze or stainless steel plates, 12 inches wide, 43 inches long, and about $^{3}/_{8}$ inch thick, containing slots ranging from 0.006 to 0.010 inch in width, usually referred to as 6-cut, 10-cut, etc. Plates are mounted in the same plane slightly inclined to the horizontal in a long trough. Below the plates are vibrating rubber diaphragms. The screen depends for its operation on a combination of gravity flow and suction from the diaphragms.

Rotary screens vary widely in design and operation. Some types consist of either fixed or stationary horizontal perforated cylinders with rotating paddle wheels in the center. Stock is fed into one end of the cylinder and is forced along and through the screen section which may or may not be graduated. Accepted stock passes through the screens.

At the Lebanon mill there are 10 flat screens, each consisting of 12 plates. Five screens are in each of two lines arranged in U-formation. The slots run from 6- to 12-cut, the plates having the larger slots being near the receiving end, where the stock flows heavy; those having smaller slots are at the opposite end, where flow of stock is lighter and dirt is more concentrated. All screenings from flat screens are returned to the hammer mill after the knotter; total feed to the hammer mill is 3% of the feed.

There is also a rotary screen (*21E*) with 0.055-inch perforations. Rejected stock from the centrifugal screen is pumped to the second section of the flat screens. Accepted stock from the centrifugal screen is combined with the accepted stock from the flat screen and pumped through a series of cyclone-type cleaners. These consist of primary and secondary units which remove fine dirt left in the pulp in first screening operation (*2E*).

The Lebanon mill has experienced many advantages in screening since converting to ammonia pulping. The pulp produced here is a hard pulp (TAPPI permanganate No. 18), and formerly 4 hours were required to fine screen a cook. As a result of better penetration of the ammonium bisulfite cooking liquor and more uniform and thorough cooking, screenings have been decreased 50% and screening time to 3 hours. This has been accomplished in spite of the fact that there was a redistribution of screen plates and that more fine-cut plates were installed to screen out dirt from ingrown bark around knots that was freed as result of better penetration of the ammonium-base acid.

Conversion of Pulp to Paper Is Similar to Practice in Other Mills

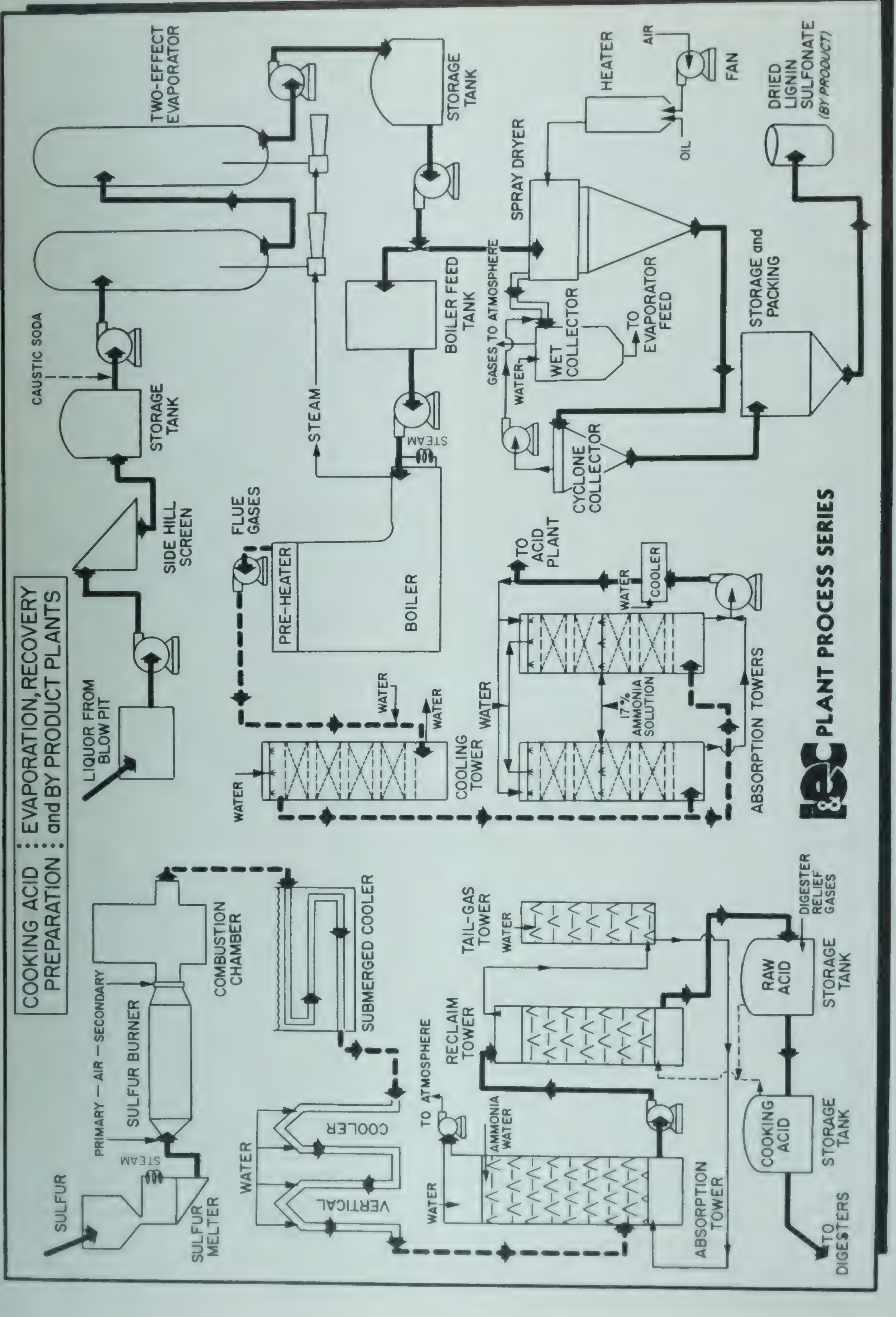
To simplify presentation, further treatment of the pulp and processing to finished paper product, which is to a great extent standard with other sulfite mills, is treated briefly in this report. The more unique acid preparation and evaporation and use of cooking liquor are then described.

Thin pulp from the cyclonic cleaner has a consistency of only 0.2 to 0.4%, and this must be increased to $3^{1}/_{2}$ to 4% on a stock thickener (*4E*).

A thickener is essentially a wire mesh-covered cylinder rotating in a vat containing the thin screened stock. The pulp adheres to the rotating screen surface while the water passes to the inside of the cylinder and flows to the white water tank. The thickened stock discharges from the opposite side of the vat and is pumped to the stock storage tank. This is a reinforced-concrete tank which holds 21 tons of 3.8% pulp (bone-dry basis). The tank has a tile mid-feather, and circulation is provided by impellers in both the upper and lower parts of the tank.

From the storage tank, the pulp is pumped through a refiner (*13E*), which gives the pulp a preliminary mechanical treatment, to the beater storage tank ahead of the beaters. To this point, pulp processing has been continuous; some batch operations follow, the first of which is beating.

Beating has been considered to be a major part of the transition between pulp and paper. Various types of equipment have been used in the industry for beating, during which the various components of the furnish are added, the pulp is hydrated, and the surface character of the fibers is changed. The expression, "paper is made in the beater," has long been associated with the functioning of the Hollander beater, which was first used. However, many mills have substituted other types of equipment to perform this operation.


COOKING ACID PREPARATION : EVAPORATION, RECOVERY and BY PRODUCT PLANTS
SULFUR
SULFUR MELTER
STEAM
PRIMARY — AIR — SECONDARY
SULFUR BURNER
COMBUSTION CHAMBER
SUBMERGED COOLER
VERTICAL COOLER
WATER
TO ATMOSPHERE
AMMONIA WATER
WATER
ABSORPTION TOWER
RECLAIM TOWER
TAIL-GAS TOWER
WATER
DIGESTER RELIEF GASES
RAW ACID
STORAGE TANK
COOKING ACID
STORAGE TANK
TO DIGESTERS
LIQUOR FROM BLOW PIT
SIDE HILL SCREEN
STORAGE TANK
CAUSTIC SODA
TWO-EFFECT EVAPORATOR
STORAGE TANK
STEAM
BOILER FEED TANK
STEAM
FLUE GASES
PRE-HEATER
BOILER
WATER
WATER
WATER
COOLING TOWER
WATER
17% AMMONIA SOLUTION
WATER
COOLER
TO ACID PLANT
ABSORPTION TOWERS
SPRAY DRYER
GASES TO ATMOSPHERE
WATER
WET COLLECTOR
TO EVAPORATOR FEED
CYCLONE COLLECTOR
HEATER
OIL
AIR
FAN
DRIED LIGNIN SULFONATE (BY PRODUCT)
STORAGE and PACKING
I&EC PLANT PROCESS SERIES

At Lebanon, hydration of the pulp occurs in the refiner. The beater is principally used to blend the added ingredients for papermaking with the pulp. This arrangement is peculiar to this mill only. Hollander-type beaters are used—three for regular pulp and one for repulping "broke," or trim, from the paper machines. The machine consists of an oval-shaped tub which holds 1200 pounds of stock (*10E*). A partition extends lengthwise through the center and at one end is a horizontal roll, 55 inches in diameter, with bars, 72 inches long, laterally positioned. The roll rotates in the pulp at 140 r.p.m. and engages a bed-plate arrangement at the bottom of the tub, permitting bar-to-bar action between it and the roll. Thorough mixing and agitation is thus provided as the pulp is circulated about the tub and through the bars.

The kind of paper being made determines the type and amount of nonfibrous raw materials to be added to the furnish. For the products at Lebanon, rosin size and papermakers' alum are added to all and aniline dyes to certain colored products. The size is added to make the paper partially water repellent; the alum, $Al_2(SO_4)_3 \cdot 18H_2O$, precipitates the size on the pulp and sets certain colors through adjustment of the pH.

In a typical beater batch, 1200 pounds of stock is first fed to the beater, which takes approximately 1 minute. Size ($1^{1}/_{2}$ to 4%) is added, followed by addition of the same amount of alum. The batch is then mixed for approximately 30 minutes and discharged into a rectangular tile-lined beater chest in the basement. The consistency at this point is 3.5%. Water is added reducing it to 3.2%. From the chest, the pulp is pumped continuously to the paper machine chest in the paper machine room.

Before the pulp becomes paper, it once more undergoes refining. Standard Jordan refiners are used at Lebanon (*11E*). The Jordan consists of a horizontally positioned conical shell which contains a rotating, correlative, cone-shaped plug. From the Jordan the thoroughly refined pulp is delivered to the paper machines by a pump to which white water is added, lowering the consistency to 0.5%. The thin stock is passed over a fine screen for removal of any dirt or heavy particles that may be present.

The balance of the conversion from pulp to paper occurs on the Fourdrinier "wire" and Fourdrinier paper machine (*14*). The entire process is one of aligning and interweaving the fibers together with dewatering to form the paper (sheets). Crown Zellerbach has two paper machines at Lebanon (*17E*, *20E*). One machine is capable of making finished paper 64 inches wide at speeds up to 450 feet per minute; the second makes paper 76 inches wide at speeds up to 520 feet per minute. Of interest is the fact that the paper machine and its auxiliary equipment are fed with stock containing 99.5% water and the finished paper leaving the dry end contains 5 to 8% water.

In Acid Making, Ammonia Is Substituted for Calcium

The Lebanon plant used a conventional milk of lime Barker system (Figure 3) when using a dolomite lime as a base. Raw materials for the Barker process include sulfur or pyrites, limestone, and water (*13*). Briefly, the Barker system consists of burning sulfur to produce sulfur dioxide gas, cooling the gas, and absorbing the gas in water in presence of lime (as milk of lime). This liquor or raw acid is calcium bisulfite. To it is added sulfur dioxide gas relieved from the digesters to obtain the fortified cooking acid. Major pieces of equipment include sulfur burners and combustion chambers, gas coolers, absorption apparatus, and equipment for strengthening the raw acid with digester relief gas. Conversion of a calcium-base plant to ammonia base is relatively simple and consists essentially of substituting an ammonia solution for the milk of lime in the Barker acid plant. At Lebanon, most of the old equipment is still used, and the principal addition to the plant is ammonia handling and storing facilities.

At Lebanon, sulfur is used as a source of sulfur dioxide gas. The sulfur is melted in a vat containing steam coils and pumped through a steam-jacketed line to the single sulfur burner. This is a conventional rotary burner, 4 feet in diameter and 11 feet long, equipped with a brick-lined combustion chamber 9 feet in diameter and 12 feet high (*8E*). A bubble-type liquid-level controller in the burner maintains the pond level within 0.25 inch and permits regulating the gas at 18 to 19% sulfur dioxide (*3E*). The gas leaving the combustion chambers is 1500° to 1600° F.; it must be cooled so the sulfur dioxide can be absorbed in water. Rapid cooling is necessary in order to prevent the formation of sulfur trioxide. A pond cooler, in which the gas passes through pipes submerged in water and a vertical lead cooler, in which water is applied to the exterior of the pipes in which the gas flows, result in an over-all temperature drop to 70° F. The cooled gas passes through an absorption tower, where it is combined with aqua ammonia to form ammonium sulfite.

Ammonia is received as anhydrous ammonia in tank cars holding 50,000 pounds. It is unloaded under its own pressure. As it flows through a pipe equipped with baffle plates, water is admitted to give a 17% aqueous solution. Rate of water flow is controlled by solution temperature rise, which is proportional to the amount of dilution. A temperature controller with a temperature bulb in the solution actuates a control valve in the water supply. Storage tanks with capacity in excess of a full tank car (reduced to 17% concentration) are available. Aqua ammonia is pumped to the absorption tower by a 5-gallon-per-minute gear pump with a hydraulic, variable-speed drive; a flow of 2 gallons per minute is used, which is checked by a recording rotameter.

The absorption tower is $3^{1}/_{2}$ feet in diameter and 43 feet high. It is divided into two sections, each of which is packed with staggered 3-inch spiral tile. The bottom section is 27 feet high. At the top of this section, water (80% of total) and the aqueous ammonia solution are added to the raw acid gas, which is admitted at the bottom of the lower section. Ammonium bisulfite and free sulfur dioxide solution are formed. Balance of water (20%) is added at the top of the upper section of the column to safeguard against losing any ammonia; this has worked satisfactorily as the water scrubs out the final trace of ammonia. Gas is pulled through the system with a stainless steel vacuum pump (*14E*).

The raw acid leaves the bottom of the absorption tower at 60 to 70 gallons per minute. It contains 2.8 to 3% sulfur dioxide—1.3% combined SO_2, the amount of sulfur dioxide that would be contained in $(NH_4)_2SO_3$ or "papermakers" sulfite. The raw acid is pumped to the top of a 4 × 20 foot wood reclaim tower. Fifteen feet of this tower is packed with 3-inch spiral tile. The acid flows from the bottom of the tower to a 25 × 18 foot (62,500 gallons) storage tank. Here the sulfur dioxide relief gases from the digesters, after passing through a tubular heat exchanger (*6E*), are bubbled up through the acid, building up the total sulfur dioxide content from 3 to 6.5 to 7%. The gases not absorbed in the mixing tank go to the bottom of the reclaim tower. The fortified cooling liquor is pumped to the cooking acid storage tank, from which it is available for use in the digesters.

The gases discharged from the reclaim tower go to the bottom of a 14-inch diameter by 15-foot high tail-gas tower packed with $1^{1}/_{2}$-inch Berl saddles. Water (8 to 10 gallons per minute) is added to the top of this tower, removing the last trace of sulfur dioxide. This goes to the bottom of the absorption tower.

Since conversion to ammonia pulping, the acid plant is almost an automatic operation. Recorders are installed on the water flow to the towers and one on the vacuum after the coolers and after the towers. Temperature and SO_2 recorders are on the sulfur burning system in addition to the liquid level control.

Before conversion, the plant replaced all acidproof bronze valves and fittings with stainless steel parts. This completed a program already under way to replace bronze parts with stainless steel as the former corroded out. Maintenance of the acid plant has been materially simplified. In addition to elimination of scale and sludge in the cooking and acid making systems, dust, characteristic of the dolomite operation, is no longer present.

After Concentration, Waste Liquor Is Burned in Plant Boilers

Following operation of an evaporation, burning, and recovery pilot plant in 1951, Crown Zellerbach installed facilities for carrying out these operations on a plant scale in 1953. Some of the results of the pilot plant operation have been published (*1, 6*).

In the evaporation, burning, and sulfur recovery system (Figure 3) spent liquors from the digesters are concentrated from 9 to 10% solids to 50% solids, burned under boilers, and sulfur dioxide in the flue gases is partially recovered by scrubbing.

The liquors from the evaporator feed sump are first pumped to a side hill screen or "save-all" which is simply a Fourdrinier wire converted into a screen inclined at 60° where remaining fibers are removed. The liquor flows to a 50,000-gallon storage tank. Another pump transfers it to the evaporator.

The concentrating plant consists of a two-effect evaporator and auxiliary equipment (*7E*). The last effect is followed by a barometric condenser. The heaters in both effects are flat-plate heaters containing 2200 square feet of heating surface. The first or high temperature effect operates as a falling film type. Operating pressure is 30 to 40 pounds per square inch. Circulation over plates is 30 gallons per minute. Condensate is circulated on the steam side of plates at 40 to 50 gallons per minute. Concentration of liquor is increased from 14 to 15% to 50% solids.

The second effect employs natural circulation. It is built exactly the same as the first effect but has a larger vapor head. There is no pump for falling film on the vapor side. The vapor passes to the barometric leg equipped with steam jet condenser, which can operate at 27 inches vacuum when necessary. The condensate from the first effect flashes to the second effect.

The entire evaporation system is piped so that the Rosenblad method of channel switching of liquid and steam plates for scale control can be employed. While the use of ammonia base eliminates scale forming materials from the cooking chemicals, there is enough calcium from the wood ash to warrant the use of this expensive channel switching equipment. Channels are switched every 8 hours on the high temperature effect and every 24 hours on the low temperature (25 pairs of valves, from $^1/_4$ inch to 16 inches must be changed each time). All plate materials coming in contact with the liquor or vapor are of Type 316 ELC or 317 ELC alloy stainless steel.

It has been found with ammonia base spent liquors that a concentration above 50% solids is not desirable. At best, there is a danger of increased viscosity which makes the liquor harder to handle and at worst, there is the possibility of an irreversible jelling due to polymerization. Some of these conditions have been reported in some detail (*6*).

The concentrated liquor goes to a 15,000-gallon storage tank from which it is pumped to a 1000-gallon wood stave tank that supplies the two boilers under which the liquor is burned. The latter tank is equipped with steam coils that maintain the heavy liquor at 190° to 200° F. The liquor has a heat content of 8800 B.t.u. per pound on a solid dry basis. As fired, it contains approximately 4500 B.t.u. per pound.

A positive displacement pump, which operates at 100 to 150 pounds per square inch, moves the heavy liquor to the burners through stainless steel pipe and metering equipment (*23E*). The burners through which the liquor is fed to one of two boilers are conventional steam atomizing burners for high pressure oil except that the liquor is on the inside and the steam on the outside; liquor discharges through a central opening and atomizing steam enters through several radial openings at right angles to it. Liquor flow to both burners is regulated by flow recorder controllers.

In the original pilot plant study, an old horizontal water tube boiler (in which the gases flow parallel to the tubes) with a dutch oven ahead of it was used. This is one of the two boilers now used in the regular plant operation. Grates were removed, and some brickwork was added to give a furnace of the proper dimensions. It is equipped with a steam preheater, a forced draft fan, an induced draft fan, and dampers for combustion control. The burner is mounted in a register in the center of the front wall of the dutch oven. Preheated air (300° F.) from the heater enters through the register in a whirling motion imparted by louvers. Flue gases from this boiler go to the sulfur dioxide recovery system when it is being used.

The second boiler has no air heater and is not equipped for sulfur recovery. It is equipped with a dutch oven for hogged fuel burning and with facilities for burning oil. It is necessary, however, to keep a hogged fuel fire going in the dutch oven inasmuch as the combustion chamber, where the liquor is sprayed in, has water walls. Liquor is burned at a constant rate, and the swings in steam demand are taken up by varying the hogged fuel feed. This boiler also accommodates fluctuations in concentrated liquor supply when the waste liquor is being disposed of in some other manner, which is described later. Each boiler handles approximately 50% of the liquor when all of it is burned.

As mentioned, one of the boilers is equipped with sulfur recovery facilities. The system consists of a cooling tower and two absorption towers which operate in parallel (one of the latter was used as a cooling tower in the pilot plant).

The cooling tower is of wood stave construction, is 8 feet 4 inches diameter and 35 feet high, and is packed with 15 feet of 3-inch spiral tile. It cools the hot gases from the burners at 450° to 100° to 105° F. Cooling water (70 gallons per minute) is added at the top of the tower and discharges from the bottom at about 200° F. Little sulfur is lost at this temperature.

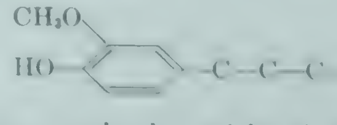
The two wood stave absorption towers (5 feet in diameter by 34 feet high) are packed with two 5-foot sections of 3-inch spiral tile. An absorption solution of ammonium sulfite-bisulfite circulates over the bottom section and is pumped through a stainless steel heat exchanger after each pass over the packing, the circulating solution containing 0.5 to 0.7% sulfur dioxide. A 17% solution of aqua ammonia is added at the suction side of the recirculation pump; feed is regulated by a pH recorder controller. Make-up water (10 to 15 gallons per minute) equivalent to the acid sent to the acid plant is added above the top section. This water removes any ammonia stripped from the scrubbing solution. A portion of the acid from the tower is taken just after the heat exchanger and sent to the acid plant where it is added to the water going to the absorption tower.

Under proper operating conditions, about 80 to 85% of the sulfur in the liquor fired to the furnace is recovered; enough steam is obtained from burning the liquor to do the evaporating. Sulfur consumption normally runs from 275 to 280 pounds per ton of pulp produced. In plants producing bleaching grades of pulp, the consumption is 240 pounds per ton.

The spent liquor is also used on streets and roads for dust control by the city of Lebanon and a number of logging companies. During the summer, this outlet represents 10 to 15% of total spent liquor production. It is also used in by-product production.

Concentrate Liquor May Also Be Used to Produce Versatile By-Products

In 1952, Crown Zellerbach announced a new commercial product produced from the concentrated spent sulfite liquor which consists of a mixture of ammonium lignin sulfonates and sugars. The structure of the lignin sulfonic acids is not known; however, it is generally believed that they are composed of repeating unit polymers of guaiacyl propane



and have an average molecular weight of 5000. The sulfonic acid group is known to be attached to an aliphatic carbon atom, probably adjacent to the benzene ring. It is also believed that one or more OH^- groups appear on the three-carbon side chain (*4*).

The material, now available in a number of grades, is produced by spray drying the evaporator discharge. The material is a light-brown powder, the particle size ranging from 0.004 to 0.006 inch diameter. It is soluble in water in all proportions and has a pH of about 3.5 in a 20% solution. Heat value is 9100 B.t.u. per pound (bone-dry basis). Water content is 3%.

The constituent analysis of the product is:

	Total Solids, %
Ligninsulfonic acids	55.0
Reducing sugars (as glucose)	16.7
Alkali-liberated NH_3	2.8
Sulfate (as SO_3)	1.6
Sulfated ash	2.0

Some potential uses of the material are summarized:

Application	Comment
Briquet and ore binder	Insolubilization with heat occurs at normal core baking period of 400° to 500° F., giving cores with high strength and water resistance
Adhesives	Compounds with fire clay to form linoleum paste
Emulsifying agent	Effective emulsifier of asphalt and oils and additives to soaps; also used as dispersant and sticking agent for agricultural sprays
Soil additive	Aggregates soil into coarse groups, aiding penetration of water and air and retention of water
Extender for other organic chemicals	Suitable for use with phenol formaldehyde
Surface active agent	Disperses fine particles in water. Useful in ceramic, cement, gypsum, ore flotation, and oil well drilling industries; also has been used in dyeing wool and paper
Sequestering agent	Strongly sequesters ferric iron, cupric copper, and stannous tin
Wind erosion preventative	Acts as cement, binding soil particles to form crust, preventing wind damage to newly planted crops; also used as road binder
Tanning agent	Gives result comparable to typical lignosulfonate (spruce extract) tanning agent

The compounds are marketed as both the ammonium salts of lignosulfonic acid and substituted sodium salts.

In making these products, stock from the concentrated storage tank is pumped at 30 pounds per square inch to the suction side of a stainless steel, high pressure, triplex pump capable of producing 5000 pounds per square inch pressure (*12E*). The pump discharges the 50% liquor into the top of a standard 18-foot diameter spray dryer (*19E*), where it is intimately mixed with incoming hot air. All parts of the dryer are made of stainless steel, Types 304 and 316. The air for drying is heated by a standard direct-fired oil burner which supplies air at 300° to 320° F. (*15E*).

The liquor is dried in suspension, the dried product (containing 4% moisture) falling to the bottom of the conical section of the dryer, from where it is conveyed pneumatically through a collecting cyclone and to the dry storage hopper (50 tons capacity) above the packing plant. Here it is filled by an automatic bagger (*22E*) into 50- or 100-pound valve-type, multiwall paper bags.

The wet gases from the dryer with some dried particles pass from the top of the dryer to a wet collector where the solids are scrubbed from the gas stream by liquor which is fed into the evaporators. Not only does the wet collector serve as a scrubber, but the heat in the gases is utilized to concentrate the feed liquor prior to evaporation. Gas and rejects from the cyclone separator are also pumped to the wet collector.

In the sodium salts of lignosulfonic acids, the ammonia ion is replaced with sodium. In making these products, caustic soda (50% solution) is added to the evaporation plant feed. The balance of the processing is the same.

Acknowledgment

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(3E) Bristol Co., Waterbury 20, Conn., liquid level controller.
(4E) Cheney Bigelow Wire Works, Springfield 3, Mass., thickener.
(5E) De Zurik Shower Co., Sartell, Minn., consistency regulator.
(6E) Electric Steel Foundry Co., Portland, Ore., ESCO cooler.
(7E) General American Transportation Corp., Chicago 19, Ill., Conkey flat plate heating surface evaporators.
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(13E) Morden Machines Co., Portland, Ore., stockmaker.
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(16E) Smith Valley Iron Works Co., Portland, Ore., wood chipper.
(17E) Smith & Winchester, Windham, Conn., straight Fourdrinier paper machine.
(18E) Summer Iron Works, Everett, Wash., double-deck chip screen.
(19E) Swenson Evaporator Co., Harvey, Ill., spray dryer.
(20E) Tanner Co., E. P., Lee, Mass., straight Fourdrinier paper machine.
(21E) Trimbey Machines Inc., Glens Falls, N. Y. centrifugal screen.
(22E) Vredenburg Development Co., Emeryville, Calif., automatic bagger.
(23E) Zenith Products Co., West Newton, Mass., positive displacement pump.

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MALTING...

Drying Kiln

ALBERT S. HESTER, Assistant Editor

in collaboration with

JOHN H. LADISH

Ladish Malting Co., Milwaukee, Wis.

BARLEY malt is the principal and one of the essential raw materials employed in the brewing of beer and ale. Malt is also an important material in the distilling and food industries. By definition, brewing is the preparation of malt beverages—that is, beverages produced by the alcoholic fermentation of the aqueous extract of malted grain.

Briefly, malting consists of steeping carefully selected barley in water to activate the dormant embryo plant in each grain, allowing the wet grain to partially germinate, and at the proper time, kilning to arrest growth. The purposes of malting are:

1. Development and enrichment of enzyme systems within the grain
2. Endosperm modification
    a. Partial digestion of protein-hemicellulose material
    b. Mild hydrolysis of starch
    c. Protein hydrolysis
3. Production of a complex product capable of yielding a predictable, uniform, and colloidally stable water extract
4. Development of the characteristic malt flavor and aroma

Flavor and other properties of the finished beer are generally affected by the type of malt used. To prepare malt of the proper enzyme content and flavoring constituents the most careful control of operating conditions for each step is necessary. Much care is exercised in the selection of each lot of grain purchased, and operating conditions are adjusted to the particular requirements of the lot of grain being malted and the type of malt desired.

The germination of barley to form malt is an industrial process utilizing the biochemical reactions of a living organism and therefore may rightfully be classified as a bio-engineering process. The use of chemical processing equipment to achieve a controlled environment for living organisms is commonplace in the fermentation industries, but malting is unique in that the organism is a species of higher plant and not a simple bacterium, yeast, or mold.

Annual domestic production of malt in 1953 was in excess of 90,000,000 bushels. Most of this went into the brewing of the 92,117,000 barrels of fermented malt beverages produced that year, although smaller quantities are used in the distilling industries and for making malt extract for food, pharmaceutical, and flavoring purposes. During World War II substantial quantities of malt were used as a converting agent in making ethyl alcohol from corn, but the process is not economical in peacetime. These other uses of malt are in addition to its use in the brewing industry. A few of the largest breweries have their own malthouses, but usually malting is carried out as a separate industry. Even when a brewer has malting facilities, he may have to purchase additional malt from a commercial maltster.

The general offices of Ladish Malting Co. are in Milwaukee, but the plant is ideally located about 50 miles west of Milwaukee at Jefferson Junction, Wis. The company has operated a malthouse on this same site for over 60 years. The continued demand for increased production has resulted in expansion of the plant to such an extent that the original, smaller plant is no longer discernible.

Barley Purchased by Ladish Is Carefully Selected

In the fall as the barley crop is maturing in the field, members of Ladish's barley staff travel through the barley growing regions to evaluate the crop. The primary midwest barley producing states are: North Dakota, Minnesota, South Dakota, Wisconsin, Michigan, Illinois, and Iowa. Hundreds of samples are collected and submitted to the Ladish research laboratory for pilot malting and pilot brewing evaluation. From the data obtained in the research laboratory it is possible to evaluate the quality of the barley before the major part of the crop moves to market. This information is used to instruct the company buyers on what types of barley to purchase and what types to avoid at the Minneapolis grain exchange and elsewhere. The quality of barley varies with different soils and different climatic conditions. The evaluation of the barley in the research department consists of physical and chemical analysis of the barley and pilot malting and brewing.

Unlike wheat, corn, and some other grains, barley for malting is not traded on the futures market. The reason for this is that Federal grades of barley are useful only for establishing general levels of value (*3*) and do not represent a true evaluation of malting and brewing quality, whereas grains traded on the futures market are interchangeable—any lot of a given grade is interchangeable with any other of the same grade. Nonmalting type barleys may produce a hazy beer or other difficulties in the brewing process.

Barley is collected from the farmers at local elevators and shipped to the grain exchange where it is sold in carload lots from samples. Ladish buyers prefer only virgin barley—that is, barley from the local elevators and not from the large terminal elevators which buy and store grain for future sale. Each lot is purchased with the understanding that it is "like sample" and is then shipped directly to the plant.

The preference for buying only virgin barley necessitates a large storage capacity, since much of the barley must be purchased during the fall of the year. The plant has a malting output in excess of 10,000,000 bushels per year, and the storage capacity for grain and finished malt is 8,500,000 bushels.

The samples of barley purchased on the grain exchange are divided into three parts, one part is kept in Minneapolis or other purchasing source by the buyers for reference, one part is sent to Ladish's main office in Milwaukee, and the third part is sent to the company's Jefferson Junction plant to be used as a comparison to ensure that the barley received is identical with that purchased. In Milwaukee the sample is evaluated and graded according to its origin, variety, moisture content, quality, and kernel size. On the basis of this information the carload is lotted to a particular bin at the plant. It is necessary to have in each bin barley that is consistently uniform.

Automatic Car Unloader Unloads Grain

Cars are unloaded by an automatic car unloader (*5E*) which tilts the car so that the grain flows by gravity from the door. An entire carload of barley can be unloaded in about 5 minutes. The grain is carried vertically 270 feet by a bucket elevator to the top of the barley head house (Figure 1). The bucket elevator has four rows of 12-inch wide buckets and is powered by a 250-hp. motor. Barley can be unloaded at the rate of 30,000 bushels an hour. At the top of the building the grain flows into a garner large enough to hold a carload of barley. As the grain runs into the garner an automatic sampler withdraws a representative sample of the barley for final check with the purchase sample. The barley flows from the garner to a hopper scale located on the floor beneath and capable of weighing a carload at a time. The sample taken by the automatic sampler is collected at the scale. The weighing operator places the sample in a pearler where the action of the rough end surface of a rotating cylinder inside of a larger cylinder with a similar surface removes the hulls. By examining the "pearled" barley the operator can distinguish any heat-damaged or other substandard grain that might be included in the shipment. Unscrupulous operators have been known to "plug" the cars of grain by placing poor quality grain in the bottom or in other parts of the car where it might not be reached in the probe sampling which is done before the car is "spotted" for unloading. By using the sampling method described "plugging" can be detected immediately. If there is any question as to the quality of the grain, the weigher can hold the questionable carload in a separate bin until a decision as to its disposition can be made.

The grain is subjected to a preliminary cleaning before storage by running it through a scalper. The scalper is essentially a double-decked vibrating screen. Large size foreign materials such as ears or stalks of grain, pieces of wood, and paper are removed by the top screen. Fine particles such as sand and noxious weed seeds pass through the bottom screen and are discarded. It is considered that storing grain in contact with such foreign matter for several months is undesirable. Also, the large foreign bodies might restrict spout openings in the materials handling system of the plant.

The grain flows from the scalper by gravity and is directed by a system of spouts to the conveyor belts which run through a long gallery at the top of the storage bins. A take-off, or tripper, from the conveyor belt directs the grain through an opening in the floor into the proper storage bin. Storage bins are large cylindrical concrete structures of the type commonly used for storing grain. The cylindrical bins are placed so that they are tangent to each other and the space between four bins forms an extra "star" bin. The interstices between cylinders on the outside edge of the building are also enclosed by walls to provide additional storage space. Bins vary in capacity from 10,000 to 100,000 bushels.

Three of a Battery of Eight Scalpers for Removing Foreign Materials from Barley

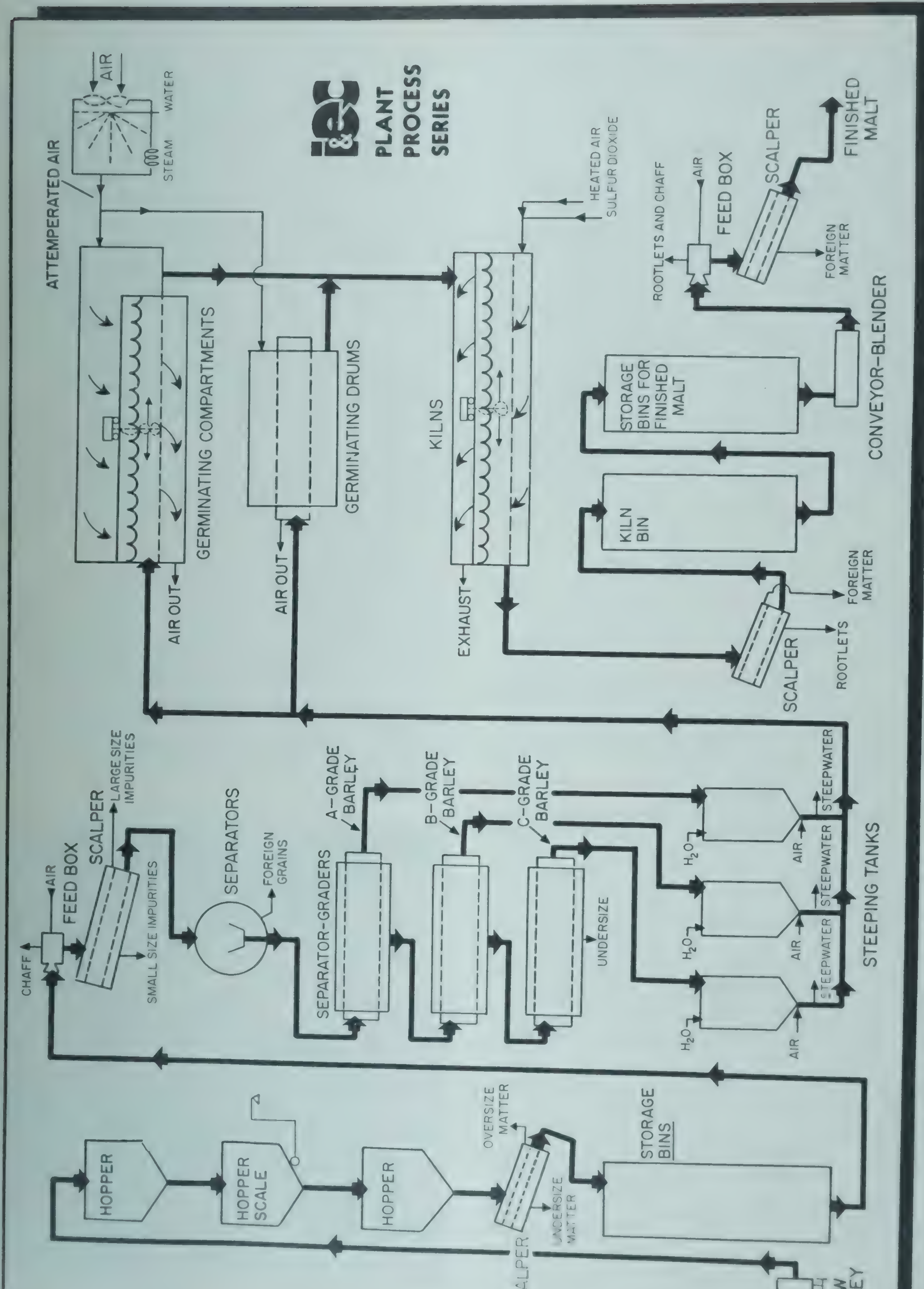
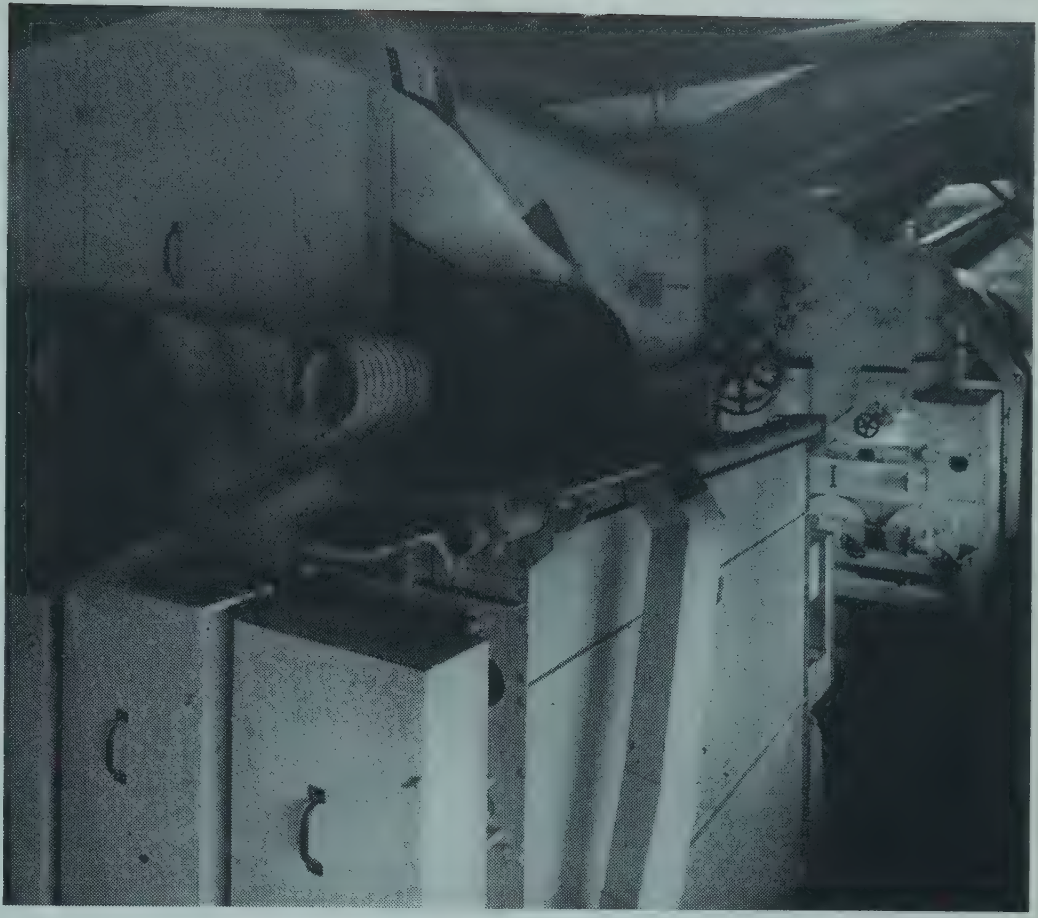

I&EC
PLANT PROCESS SERIES
ATTEMPERATED AIR
AIR
WATER
STEAM
GERMINATING COMPARTMENTS
AIR OUT
GERMINATING DRUMS
AIR OUT
KILNS
EXHAUST
HEATED AIR
SULFUR DIOXIDE
ROOTLETS AND CHAFF
AIR
FEED BOX
SCALPER
FOREIGN MATTER
FINISHED MALT
STORAGE BINS FOR FINISHED MALT
CONVEYOR-BLENDER
KILN BIN
FOREIGN MATTER
ROOTLETS
SCALPER
CHAFF
AIR
FEED BOX
SCALPER
LARGE SIZE IMPURITIES
SMALL SIZE IMPURITIES
SEPARATORS
FOREIGN GRAINS
SEPARATOR-GRADERS
A-GRADE BARLEY
B-GRADE BARLEY
C-GRADE BARLEY
UNDERSIZE
H_2O
AIR
STEEPWATER
STEEPING TANKS
HOPPER
HOPPER SCALE
HOPPER
OVERSIZE MATTER
UNDERSIZE MATTER
SCALPER
STORAGE BINS
RAW BARLEY

Figure 1. Flow Sheet for the Production of Malt at the Jefferson Junction, Wis., Plant of the Ladish Malting Co.

The temperature of the stored grain must be very carefully guarded. Thermocouples are placed at 5-foot vertical intervals in each bin. At a central control station, temperature readings of all the bins can be made. A rise in temperature as much as 1° to 2° F. is considered serious, and when this occurs the grain is aerated by transferring it to another bin.

Grain Must Be Cleaned and Graded Before Processing

Barley must be stored until it is matured since freshly harvested barley will not germinate well. Grain is stored for at least 3 months and can be kept a full year if stored under proper conditions. The first step after the barley is fully matured is cleaning and grading. Other grains and foreign material are removed, and the barley is separated into three grades based on size. Grain is carried by conveyor from the storage bins to a scalper (*4E*). In the feedbox of the scalper a stream of air carries off chaff or light material. Large size impurities are removed by the top screen, and particles such as weed seeds and sand pass through the lower screens. Magnetic separators remove stray metal that may be present in the country-run barley as received.


Separators for Removing Cracked Barley and Foreign Grains Prior to Barley Grading

The barley then flows to the separators (*3E*) which remove cracked barley and foreign grains. Each separator consists of 16 horizontal rotating cylinders whose interior walls have small indentations. A kernel small enough to find its way into an indentation is carried upward by the cylinder until gravity overcomes centrifugal force and the kernel drops into a trough running along the axis of the cylinder; in this way a size separation according to length can be made. The first series of cylinders divide the grain into large and small length grain fractions. The smaller grain drops into a second series of cylinders which have indentations of such a size that cracked barley and small grains, chiefly wheat, are removed. The larger fraction from the first cylinders goes to a third series of cylinders. Here the barley is the smaller fraction and large grains such as oats form the larger fraction. The two barley streams are reunited, and the foreign grain and cracked barley are sold for use as animal feed.

The barley, free from foreign grains and other impurities, is now ready for separation, according to the kernel width, into three separate malting grades and undersize. Undersized material is not malted but is sold for cattle feed. Separation into lots of uniform grain size is necessary for proper control of later processing steps. For example, a longer steeping time is needed for the larger kernels to absorb sufficient water to reach the proper moisture content.

Size separation is accomplished by three series of width-separation graders (*6E*) designated *A*, *B*, and *C*. These graders are horizontal, rotating, cylindrical screens. Screen openings are uniformly spaced slots around the circumference of the cylinder. Slot width is the critical dimension, and individual grains are classified according to their width. Barley is introduced at one end of the cylinder, and oversize flows out the other. *A*-grade grain would be the oversize from the *A*-graders. Undersize from the *C*-graders is that portion discarded for sale for feed purposes. *C*-grade malt, from the standpoint of kernel size, is usually used by distillers and *A* and *B* by brewers.

Steeping Activates Dormant Embryo in Each Grain

The graded barley is now ready for steeping in water. During the steeping process the grain absorbs moisture, and the dormant embryo in each grain becomes activated. Steeping is carried out in large open cylindrical mild steel tanks with conical bottoms. These tanks are of two different sizes depending upon the germination facilities they supply. The larger tanks have a capacity of 1850 bushels of steeped barley, and the smaller tanks contain 700 bushels. Respiration, one of the physiological processes of steeping barley, demands a large supply of oxygen for the grain. This is supplied intermittently both by draining the water from the tank and refilling it or by introducing air into the tank. Exact procedure varies depending on the barley and type of malt wanted.

Steeping time varies from 50 to 70 hours. Generally speaking, the grain is under water about twice as long as it is exposed to air. The first water becomes quite dark as it removes much of the tannins, bitter resins, and some of the proteins. The bitter resins and tannins adversely affect the flavor of the malt. Steeping temperatures are held between 50° and 60° F.

Steeping is continued until the moisture content of the grain reaches a specific value between 45 and 47%. Activation of the embryo will take place when the moisture content is as low as 25%, but germination does not proceed normally at this low moisture level. The danger of oversteeping is that respiration of the embryo is inhibited resulting in a larger percentage of non-germinating or abnormal germinating kernels. After steeping the barley is transferred to the germination facilities.

Germination is the reactivation of the growth of the embryo which was arrested at the ripening of the seed. The center of growth is the germ, located at the proximal end of the kernel. From the germ the acrospire grows on the dorsal surface within the husk or lemma, toward the distal end. Rootlets arise from the germ and emerge from the proximal end of the kernel. The acrospire is the embryonic structure of the germinating kernel which normally develops into the mature plant structures found above the ground. During germination, the many important biochemical changes that convert raw grain to malt take place.

Strict moisture and temperature control must be maintained during germination. Germination is now usually conducted by one of two methods—drum method or compartment method. The drum method requires a higher investment initially, higher operating costs, and maintenance costs. The quality of malt is the same in each case, and both systems are employed by Ladish. The newer portions of the plant use the compartment method.

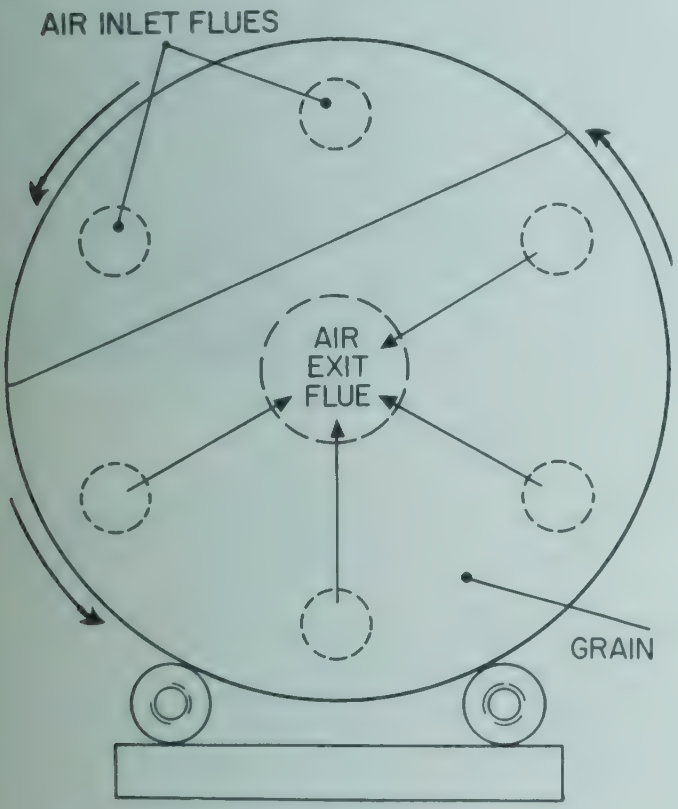


Figure 2. Cross Section of Germinating Drum

For drum germination, steeped grain is placed in large rotating cylinders (*1E*). Attempered air of 100% humidity, at a predetermined temperature between 50° and 60° F., flows through the drums. A cross section of a drum is shown in Figure 2. Inlet and exit flues are slotted tubes running the length of the cylinder. Air enters the inlet flues, flows through the grain, and out the center exit flue. A weighted damper in the head of the drum blocks off those inlet flues not covered by grain. The drums rotate at a rate of about one revolution each 40 minutes. The air supply is obtained by drawing outside air into the system by large fans. The incoming air passes through a chamber into which cold artesian well water is sprayed to provide the humidity and cooling. Temperature is maintained by low pressure steam coils in the winter. Samples are taken from each drum each day to evaluate the progress of the germinating barley so that conditions for the next day's operation can be established. The conditions varied are chiefly the temperature and air volume. Evaluation is based on moisture content, texture of the endosperm, and the length to which the acrospire has grown. The acrospire, in properly germinating barley, grows to a point between three quarters and the full length of the kernel in 6 days. Both rootlets and acrospire grow at the expense of endosperm proteins and carbohydrates. Therefore their growth must be properly controlled to obtain maximum carbohydrate yield.

In compartment germination the steeped barley is placed in long compartments about 15 feet wide, 5 feet deep, and 135 feet long. The floors of the compartments are constructed of slotted screens that permit attemperated air, forced into the compartment room, to flow through the grain and out through a duct beneath the compartment. At intervals the grain is turned by a turning device (*2E*) consisting of several augerlike stirrers operated by electric motors. These are mounted on a carriage which straddles the compartment and slowly moves from one end of the compartment to the other and back again. Attached to this carriage is a water sprayer for maintaining the proper moisture level within the grain.

The germination period is 6 days. The germinating compartments are so constructed that one end of the compartment is both removable and accessible. The flooring adjacent to the removable end of the compartment contains a grating that opens to a conveyor below the floor. At the end of germination the end of the compartment is removed and, by means of a wooden scoop, operated from a powered cable and winch, the "green" malt is transferred from the compartment, through the metal grating onto the conveyor to the kiln. In the kiln the moisture content of the malt is reduced from about 45% to approximately 4%. The purpose of kilning in addition to reducing the moisture content is to stop germination and to further develop the aromatic and flavor characteristics of the malt. The kiln is similar in construction to the compartment except that it is wider and the depth of grain is greatly reduced. It also has turning equipment (*2E*). Heated air is drawn upward through the kiln.

Kilning usually takes either 2 or 3 days. Kilns are arranged with either two or three floors depending upon the type of equipment used and the type of malt being processed. Heated air is passed upward through the lowest kiln and on up through the upper kilns. Green malt is placed first in a kiln on the top floor. After one day it is dropped through the floor to the kiln below by tipping the pivoted trays that make up the floor of each kiln. Tipping is manual; individual levers along the side of the kiln operate each tray. For a time as the malt is being finished, temperatures of 180° F. on the lower kiln are applied. By-pass facilities are provided so that temperatures of the more moist malt on the upper kilns may be held at the required low level. Temperature is measured by thermocouples placed throughout the kiln. Sulfur dioxide is introduced into the air stream passing through the malt for 15 minutes each day. Sulfur dioxide serves as a bactericide and fungicide for surface organisms that the grain may have acquired from the soil. Treatment of the malt in this manner does effect a moderate bleaching of the husk of the malt. The rootlets formed on the grain become dry and brittle during kilning and break off. From the kiln the grain is sent through a scalper (*4E*) to remove the sprouts. These are separated and sold as a valuable dairy feed.

Following the scalper the malt from each kiln goes into a kiln bin where each individual kiln lot is kept separate; each kiln has its own bin. As the malt enters the kiln bin samples are withdrawn and submitted to the control laboratory for complete chemical and physical analysis. On the basis of this analysis the contents of each kiln are lotted to the appropriate bin where malt of similar properties is stored. Malt must age a minimum of 4 weeks in the aging bins.

Malt is shipped to customers in carload quantities, and each carload is blended individually to the customer's requirements. The customer orders malt of given specifications which might include kernel size assortment, varietal composition, extract yield—that is, amount of soluble material—diastatic power, alpha-amylase, ratio of soluble to total protein, wort color, and many others (*1*). The proper blend required to meet specifications is calculated using the analyses of the various lots of malt on inventory. Most blends contain malt from eight to ten different lots. Each storage bin is equipped with a calibrated "bin-slide" valve permitting rapid adjustment for accurately controlled proportional flow of malt. In this way grain flows from the selected bins at rates proportional to the amount of grain desired in the final blend. The blended malt is run through a scalper to remove any foreign matter and over a magnetic separator for the removal of stray metal. It is then weighed and run directly into boxcars. Before release, physical and chemical analysis of the average loading sample is conducted for control of compliance with customer specifications.

Chemistry of Malting Process Is Complex

The chemical changes occurring during malting are complex. Meredith and Anderson (*4*) have reviewed the current status of our knowledge of this subject.

Barley and malt contain about 70% carbohydrate material, mainly starch. During malting the cell walls of the starch-containing cells are digested by the malt enzymes. The percentage of cold water solubles, which are mostly nonstarch carbohydrates, increases from 10% in barley to 20% in malt. The water extracts contain raffinose, maltose, sucrose, galactose, dextrose, fructose, arabinose, xylose, ribose, and uronic acids. The concentration of sugars in malt is about four times that of barley. Degradation of the cell wall permits the amylases to liquefy and hydrolyze the starch of the malt during the "mashing" process in the brewery.

The chemistry and roles of the α- and β-amylases are better known to the maltster and brewer than are other enzyme systems. β-Amylase exists in barley as both a soluble and insoluble component. The insoluble β-amylase is rendered soluble through the malting process. The α-amylase content of barley is negligible, but it increases during malting. Proteolytic activity and power also increase during malting. The proteins of the endosperm matrix are hydrolyzed for resynthesis within the expanding acrospire. High molecular weight protein degradation to the lower molecular weight fractions is desired by the brewer for producing a colloidally stable beer.

Ladish Generates Own Electric Power

Ladish's malting plant has its own electric generators. Ordinarily steam from 400-pound coal-burning boilers operates turbines which rotate the generators. Exhaust steam from the turbines is used for heating. Because of the disasterous effects that might occur in case of a power failure, additional boilers and turbines give a 100% stand-by capacity.

Water for the plant is drawn from nearby wells. Temperature of the water is very important. The availability of a plentiful supply of cold water was one of the main reasons for locating the plant at the site it occupies. Discarded grain and malt sprouts are sold as feed. Steep water, the main waste product, is effectively handled by running it through a trickling filter type sewage disposal plant. Raw grain is brought into the plant and malt shipped out by rail.

Malting Practiced in Ancient Times

Malting and brewing are ancient arts. In the early days most malting was carried out by the floor method, but floor malting is now an obsolete practice in this country. Floor malting is still followed extensively in Europe, although more modern techniques are also employed. In a recent article Thomson compared the different malting methods (*7*). In floor malting grain is removed from the steep tanks and spread on floors to germinate. The floors are ordinarily stone, concrete, or tile, and a malthouse usually has several stories of such floors. The grain from the steeping tanks is usually piled into a "couch," 16 to 20 inches

Some of the 114 Germinating Drums

Ladish also has compartment germination not illustrated. In germination, embryonic plant in each grain starts to develop. Attemperated air of 100% humidity flows through the drums at carefully controlled temperatures; germination period is 6 days.

Steep Tank Aeration

thick, and allowed to stand for perhaps a day until the temperature rises to about 60° F. Then the grain is spread in a thinner layer, 3 to 6 inches deep on the floor. It is turned occasionally by hand to ensure uniform germination. Length of time of germination varies from about 8 to 10 days. For a malthouse such as this, air is supplied by opening the windows. Weather has an important effect on the germination. The process can be controlled to some degree by opening or closing the windows and by varying the depth of the grain on the floor. In warm weather the layer is made quite thin and in cooler weather the barley is spread in a thicker layer. These means of control are not sufficient to ensure proper germination conditions during the entire year, and in this type of malthouse malting is a seasonal operation confined to the cooler months. Not only germination but also steeping time is affected by the weather.

Through installation of air-conditioning equipment the European maltster has somewhat relieved his floor malting system from dependence on weather conditions.

In England the products from combustion of coke or anthracite coal are introduced directly into the kiln. Elsewhere and in the United States heated air is generally employed. High kilning temperatures produce malt giving a darker beverage. Various darker beers and ales are popular abroad, but for the most part the preference in this country is for pale beer and ale.

Although barley is the most important cereal malted, other grains are sometimes malted also (*5*). Wheat malt is used in conjunction with barley malt for some types of beer. Rice malt is sometimes used, especially in Canada.

Pilot Malting and Brewing Are Best Means of Evaluation

Malt is an intermediate material for the manufacture of a highly complex product. Malt evaluation has been reviewed by Becker and Siebel (*2*). Although many tests and analyses help in predicting the behavior of malt in the brewery, a really satisfactory evaluation is achieved only by examining the end product, beer. The trend in the malting and brewing industries is toward more and more pilot scale brewing.

Ladish has in operation a laboratory with pilot scale equipment for both malting and brewing. It is one of the most complete laboratories of its kind in the industry. Barley evaluation, process modifications, and varietal differences can be examined more scientifically by means of the pilot plants. Pilot equipment also enables the company's research staff to collaborate with customers on specific problems.

The pilot malthouse consists of a steeping unit, a germinating unit, and a kiln. The steeping unit is a stainless steel cabinet 8 feet long, 4 feet wide, and 3 feet tall. Access is through glass doors on the top of the cabinet. Two-pound samples of barley are placed in stainless steel cylinders about 6 inches in diameter and 18 inches tall with screened bottoms. These cylinders are placed in a rack in the cabinet so that they are immersed into one of three thermostatically controlled water baths. Draining is accomplished by lifting the cylinder. If special steep waters are being studied, cylinders with solid bottoms are used, and draining is accomplished by decantation.

A cabinet similar in size to the steeping cabinet is used for germination. The unit contains spaces to accommodate the same type of cylinders used to hold the barley during steeping. Each space holding a cylinder is surrounded by a warm water jacket so that temperature may be controlled. The 2-pound samples used are not large enough to hold heat generated, and the temperature does not rise of its own accord as it does in full scale operation. Attemperated air flows through a duct into the top of the cabinet and down through the cylinders. Flow through each cylinder is controlled by dampers placed beneath. After flowing through the cylinders the air is discharged to the atmosphere or recirculated. The top surface of the rack with openings for the cylinders is made in the form of a 1-inch thick cold water jacket to prevent the air entering the germinating unit from becoming heated by the warm water jackets before it passes through the grain.

The kiln unit is similar in appearance to the first two units described, except that the cylinders used to hold the malt are of a different size—3 inches in diameter and 2¹/₂ feet tall. The depth of the grain in the cylinder is the same as the depth in a commercial unit. Air entering the kiln is heated by an electrical coil and passes up through the first row of cylinders, down through the second, and up again through the third. Sulfur dioxide from a gas cylinder can be introduced into the air stream when desired. With these three units it is possible to duplicate commercial scale processes almost exactly.

Pilot Brewing Parallels Commercial Process

The next logical step in evaluating malt from the pilot or commercial plant is pilot brewing. Modern brewing practices have been described by Vogel and associates (*8*) and a particular commercial brewery operation reported in this series (*6*). Ladish's pilot brewing facilities consist of two identical brewing units so that a control brew can be made for comparison in conjunction with a test brew. Each unit of the pilot brewery has a capacity of 5 gallons of wort per brew. The cereal cookers, mash tubs, lauter tubs, brewing kettles, hop strainers, and wort tanks for both systems, together with the cooler common to both, are mounted on the wall of the laboratory. Wherever possible equipment was constructed from stainless steel. The wall and floor beneath are covered with tile for ease of cleaning. Water recirculation and temperature control equipment are placed in a separate room behind the wall upon which the equipment is mounted.

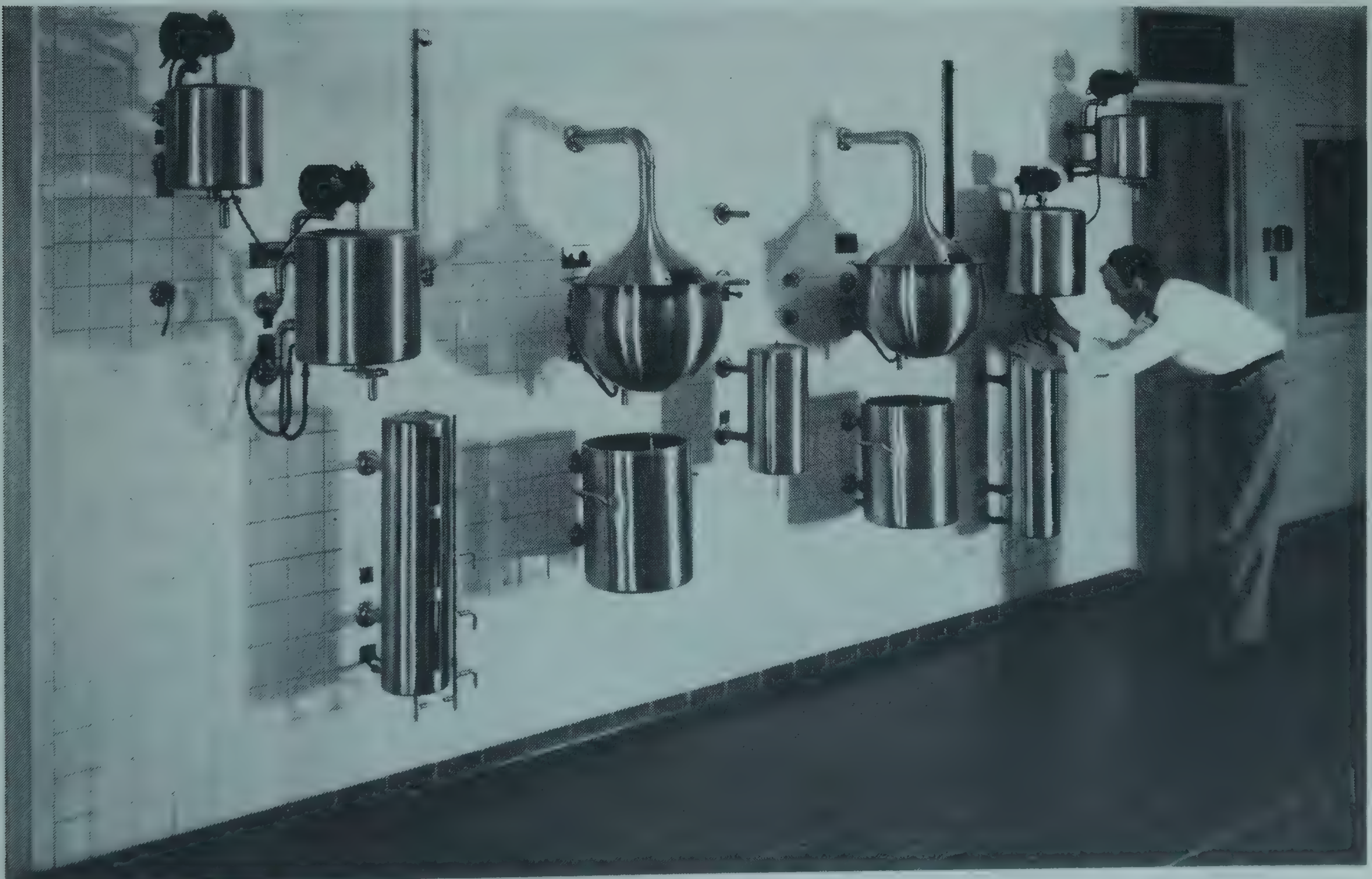
Brewers normally supplement malt with cereal "adjuncts" such as corn or rice. The adjunct plus a small portion of the total malt to be used is ground and boiled with water in the cereal cooker, a vessel fitted with steam coils for heating. This boiling process is employed to solubilize the starch in the adjunct.

The bulk of the malt is ground and mixed in warm water in the mash tub. The mash tub is equipped with water coils for attemperation and an agitator for thoroughly mixing the adjunct and malt during conversion, thus ensuring complete starch hydrolysis. The "mashing" operation is divided into two phases:

1. Peptonization: During this phase the malt alone is infused in water to disperse enzyme systems and permit protein hydrolysis.
2. Conversion: Liquefied adjunct from the cereal cooker is combined with the malt infusion, and the combined starches are hydrolyzed to dextrins and fermentable sugars.

The temperature employed for conversion determines the degree of hydrolysis and thus the ratio of fermentable to nonfermentable extract. It should be noted that the diastase is derived entirely from the malt and is sufficient to hydrolyze the combined starches of malt and adjunct.

Following conversion the mash mixture is transferred to a lauter tub where the water-soluble materials are extracted. The lauter tub is a cylinder about 6 inches in diameter and (to simulate the depth of grains in commercial lautering procedure) 2¹/₂ feet tall with a perforated plate forming a false bottom. The malt husks



Pilot Brewery

Ladish has two identical brewhouse units with a cooler between: from left to center, the cereal cooker, mash tub, lauter tub, and brewing kettle with hot wort tank below it.

A Corner Showing Portion of Lab Mashing Equipment in the Ladish Control Laboratory

act as a filter medium for the wort which is drawn off. Sight glasses enable the operator to note the depth and degree of settling of the mash in the lauter tub.

The wort flows into the brew kettle where it is boiled with hops. Hops impart a characteristic flavor and aroma to the wort. Also, boiling with hops precipitates some of the proteins and removes other materials. The brew kettle is a small replica of the large kettles used in commercial breweries. It is stainless steel and roughly ovoid in shape. There is a rounded more-or-less conical indentation in the bottom. This shape affords a nucleus for an excellent boiling action.

After boiling is completed the hops are removed from the wort by the hop strainer in the top of the hot wort tank. Hot wort is conducted through the cooler where brine coils reduce the temperature. Cool wort is placed in stainless steel vessels and inoculated or "pitched" with yeast. Fermentation takes place in a cooled fermenting room where the vessels stand in a cooling bath with temperature controlled precisely.

After fermentation the beer is decanted from the yeast and aged for approximately 1 month. After aging the beer is filtered to remove precipitated proteins and any remaining yeast. The finished beer is then carbonated, bottled, and pasteurized. Evaluation of all phases of the brewing process as well as the quality of the finished beer is possible with this type of equipment. The pilot brewing and malting installations together with the accompanying testing laboratory permit as nearly complete an evaluation of barley and malt as is possible.

Research Is Directed Toward More Uniform Malt of Predictable Qualities

Research at Ladish is directed not only toward production of a better malt but also toward processing a product of further improved uniformity whose performance in the brewery can be predicted with a greater degree of accuracy. Valuable returns from money spent on research by the malting and brewing industries is being obtained from pilot brewing work. Substantial progress in the resolution of fundamental, practical problems of malting and brewing technology is now being made by the brewer and maltster through the use of pilot malting and brewing equipment. Research is also being done by such organizations as the Malt Research Institute of Madison, Wis., to develop improved strains of barley.

The consumption of beer will probably continue to increase with the population, and it is possible that per capita consumption may increase as well. There is every reason to believe that beer will continue to grow in popularity in this country, and malt consumption and the use of agricultural products which go into its production will continue to rise.

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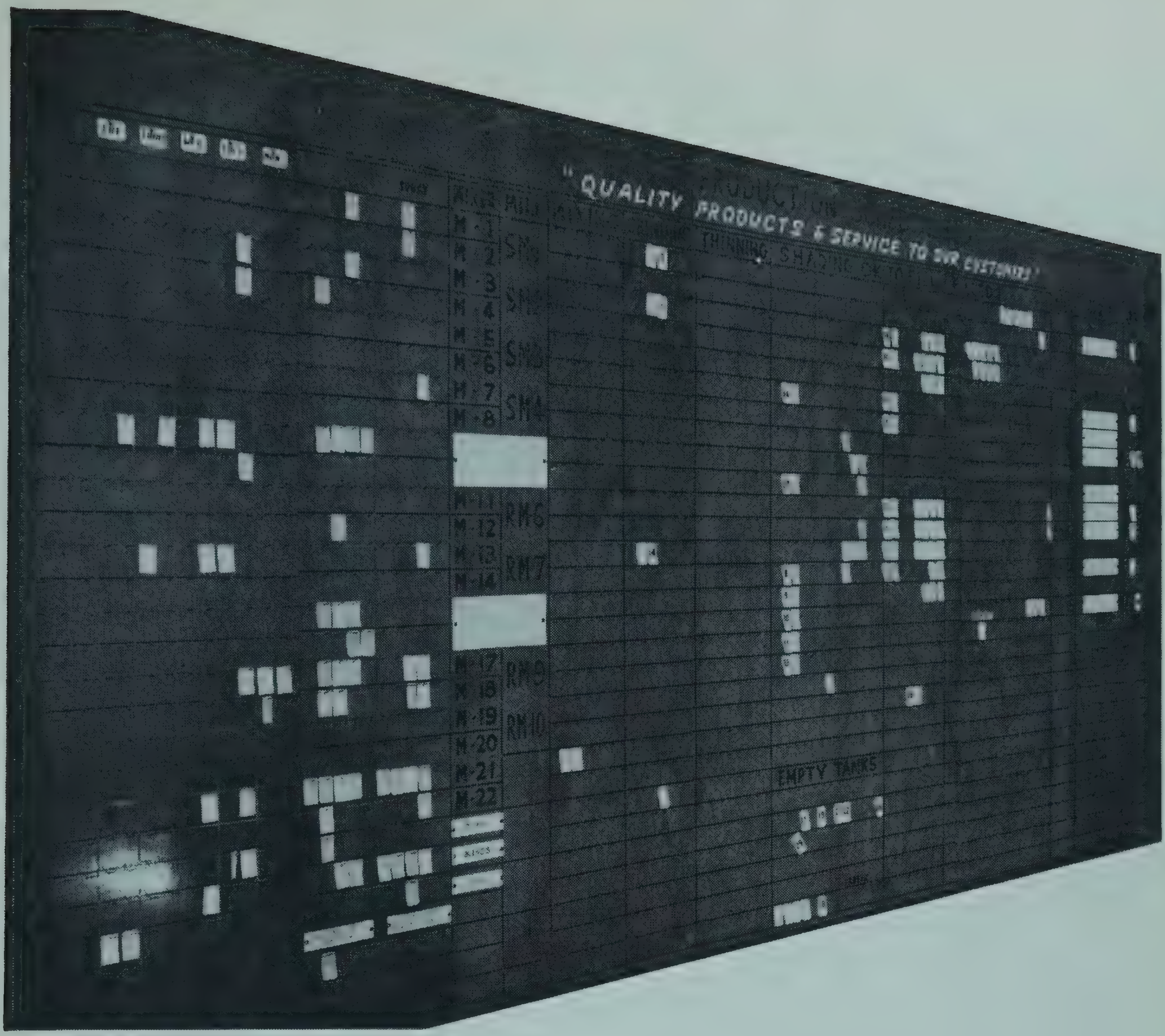
Processing Equipment

(1E) Galland Henning Mfg. Co., main office, Milwaukee, Wis., germinating drums.
(2E) *Ibid.*, turners.
(3E) Hart-Carter Co., Minneapolis, Minn., No. 32 precision grader.
(4E) Howes, S., Co., Silver Creek, N. Y., Eureka No. 15 scalpers.
(5E) Link Belt Co., Chicago, Ill., automatic car unloader.
(6E) Superior Separator Co., Hopkins, Minn., separators.

This article appeared in Vol. **46,** *page 1738 (September, 1954).*

Ladish Malting Co., Jefferson Junction, Wis.



HARRY W. HAINES, JR.
Associate Editor

in collaboration with

DON GRIFFIN AND A. J. DAVALLE
DeSoto Paint & Varnish Co., Garland, Tex.

Resin and Paint Production—1954 Style

PAINT manufacturing, for centuries an industry using techniques almost esoteric, has gradually evolved into an operation heavily dependent on and of major interest to chemists and chemical engineers. Today at least five unit operations are common to almost all paint factories—mixing, grinding, reducing and tinting, filtering, and packaging (*16*). On the basis of chemical employment, paint factories can boast impressive figures, exceeded during 1953 only by those for the manufacture of industrial organics and inorganics and the manufacture of drugs and medicines. Last year the paint industry accounted for more than 9% of the total employment in the production of chemicals and allied products (*6*).

Dollar volume of sales in this important chemical processing and chemical consuming industry hit a new record of \$1.4 billion last year (*17*) compared to \$1.34 billion in 1952. The new figure is more than three times that for paint, varnish, and lacquer products marketed in 1939.

Technology is playing a much more important role in paint production than ever before, contributing in no small measure to the market growth indicated in Table I. Although most plants still use many of the standard mills and mixers that long ago became traditional (*10*) and essentially all use pebble and steel ball mills in addition to three- and five-roll mills, several U. S. factories have in recent times adopted the British single-roll mill with satisfactory results. As a result of technological progress, very few of the old type, flat buhrstone mills are found in operation. Numerous attempts have been made to develop some sort of colloid mill or homogenizer for dispersion purposes but without any reasonable degree of success with the average material.

Developed for the most part during and after World War II, high speed stone mills are now manufactured commercially by several equipment vendors. These mills occupy little floor space and are relatively small and light; they have extremely high production rates and can be moved about the plant on wheels. If properly used the mills produce excellent dispersions.

In the latest plants there is a definite trend toward the use of larger paste mixers, ranging from 200- to 300-gallon capacity, and larger thin-down tanks with capacities of 1000 gallons or more. This development is particularly evident in plants where production of large runs can be scheduled and where the mixers and thin-down tanks can be tied in with operation of high capacity mills such as the high speed stone mill or a high speed three-roll mill.

On par in importance with improvement and more effective use of existing equipment is a universal industry interest in reducing labor costs. Production of larger batches is one step in this direction, augmented by more efficient materials handling systems. The postwar paint plant has turned to increased use of palletized storage, both of raw materials and finished goods. Conveyors, automatic filling and labeling machines, automatic carton closing machines all are being employed to maximum advantage.

A controversy still exists as to whether paint plants should be single or multistory structures. However, most recent ones have been multistory buildings that depend on gravity flow of materials throughout.

Among segments of the industry, varnish and resin production have probably experienced the greatest advances. To keep pace with changing markets, most large plants now insist on having their own resin facilities for maximum flexibility in the manufacture of the paint plant's vehicles. As in paint plants, the trend here is toward larger batches. Many installations have kettles with capacities in the 1000- and 2000-gallon range; a few large manufacturers have kettles of even greater capacity. In combination with stationary thin-down tanks, large volume production has led to decreased operating cost.

Air pollution abatement has become the byword of almost all chemical industries, including resin manufacture. In this field the paint industry has made serious attempts to eliminate undesirable fumes formed during the manufacture of bodied oils, alkyd resins, and varnishes. Dilution of effluent vapors with air, incineration, and water scrubbing have all been tried; results have ranged from moderately to completely successful. Probably the best and most recent method is that of prescrubbing exhaust gases with a mixture of oils and fatty acids condensed from the vapor itself, followed by water scrubbing (*2*). Jet contactors and spray towers are becoming popular in this development.

DeSoto Has Newest Paint-Resin Plant in the South

The DeSoto Paint & Varnish Co. plant at Garland, Tex., is typically modern and employs most or all of the innovations described. As a member of National Affiliates (owned by Sears, Roebuck & Co.), DeSoto has five sister organizations—Benjamin Franklin Paint and Varnish Co., Philadelphia, Pa., Illinois Paint Works, Chicago, Ill., Pacific Paint & Varnish Co., Berkeley, Calif., John A. Steen Varnish Co., Chicago, Ill., and Carolina Paint & Varnish Works, Greensboro, N. C. All members of this group produce both trade sales items and industrial finishes for consumers, industry, and government.

DeSoto was founded in 1901 as the Memphis White Lead & Color Works, with fewer than 30 employees. In 1921, the company was purchased by Barron G. Collier, and its name was changed to DeSoto Paint Manufacturing Co. The latter was forerunner of the present organization, renamed in 1929 following its purchase by Sears.

The company's Garland plant, employing more than 130 workers and utilizing the latest in paint technology, is the direct result of continual improvement and expansion. For some years, DeSoto had upgraded its installation at Memphis, Tenn., by replacing obsolete facilities and adding new production units. Eventually, however, the scarcity of suitable space for further expansion at the Memphis site, coupled with the DeSoto management's growing confidence in the Southwest as a desirable location for chemical processing operations, led to a decision to erect a completely new plant. Since over 50% of DeSoto's production had been moving into the Dallas area, that area was easily selected as the proper locus; after examination of many possible plant sites over a period of months, DeSoto officials settled on the present 20-acre site at Garland.

Table I. Paint, Varnish, and Lacquer Sales in the United States[a]

	Millions of Dollars		Millions of Dollars
1939	444	1947	1194
1940	464	1948	1207
1941	617	1949	1107
1942	589	1950	1327
1943	631	1951	1339
1944	687	1952	1341
1945	716	1953	1403
1946	883		

[a] Source: National Paint, Varnish and Lacquer Association

The result, a multimillion dollar paint and resin plant, one of the South's largest and one of the most modern in the United States, began operations on October 18, 1953. Located on the western outskirts of Garland, just 15 miles northeast of downtown Dallas, the plant encompasses 145,000 square feet of manufacturing and warehouse area. All buildings are of concrete, brick, and steel construction throughout, designed for 50% expansion without interruption of production.

The paint factory proper is a three-story steel-reinforced structure designed for gravity flow of materials. When officially opened, the plant was rated at a capacity of 1,500,000 gallons of paint annually, based on single-shift operation. By adding an extra shift, some operations could be doubled without adding equipment; to double total output, however, additional ball and pebble mills would be required, since most of these already operate around the clock. Sufficient land and utility resources are available to increase production to 8,000,000 gallons per year, if required.

The resin plant, also of brick and steel, is essentially a single-story building, although part of its equipment is situated on a mezzanine. The building's floor plan provides for doubling capacity without disturbing present facilities.

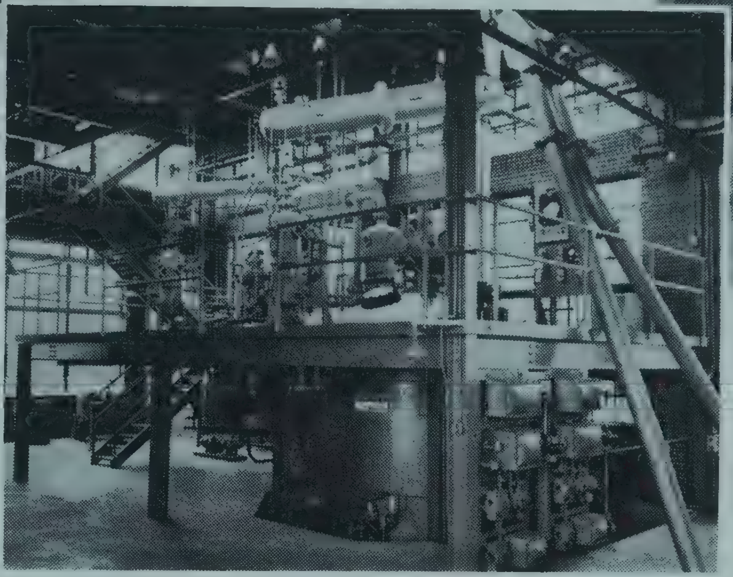
DeSoto's tank farm for liquid storage, which feeds supplies to both the resin and paint plants, has a capacity of 300,000 gallons and is totally enclosed in a separate building for temperature control. Tanks are of rectangular construction to conserve space; additional tanks to handle expanding production needs can be installed directly above those already in place. Adjacent to the storage area is a room housing complete pumping facilities for moving fluid raw materials by pipeline directly to the processing areas.

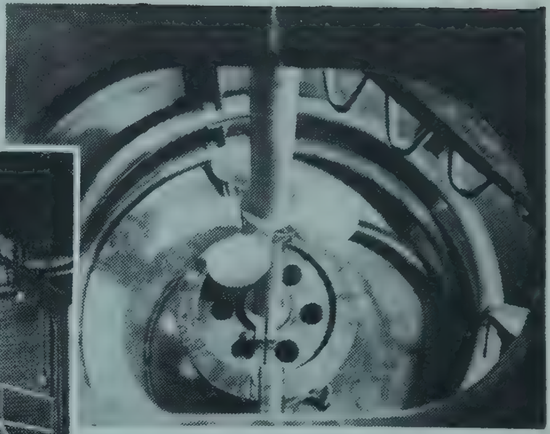
A single storage tank, with its own temperature-controlled building behind the paint plant, is provided for storage of 10,000 gallons of latex used in formulation of rubber-base paints. The tank is Heresite-lined for protection against corrosion and is connected by stainless steel lines to the processing area in the paint factory.

Space is provided on the first floor of the paint plant building for storage of bulk solid raw materials; from this point, supplies are moved in smaller quantities and spotted as needed at secondary storage areas near production units on the third floor.

Steam ejectors on top of resin plant pull a vacuum ($3^1/_2$ inches of water) and remove by-product vapors from reactors

Two batch reactors in resin plant process 2500- and 250-gallon charges; entire electrical system is explosionproof





Reactors are equipped with foam breaker and agitator; water cooling coils maintain isothermal reaction conditions

Resin Production

A part of the bulk materials warehouse roof is concrete, an extension of the paint factory's second floor. Now used for drum storage of liquids, this area could eventually be enclosed to provide additional manufacturing area. If the third floor were extended and enclosed in the same way, 40% additional production could be accommodated. In that event, new raw material storage facilities would be constructed on ground adjoining the present storage area; space has been specifically allocated to this purpose.

An extensive single-story main warehouse building to the north of the paint plant provides facilities for receiving raw materials and for storing and loading finished goods. Individual hydraulic levelers permit adjustment of dock levels to meet truck beds. Maximum use is made of pallets to speed operation and lower costs. Most solid materials shipped to DeSoto are in prepalletized unit-load form to expedite handling.

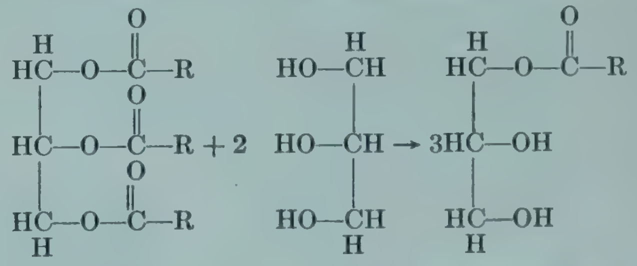
Completing the cluster of buildings is the two-story main office building adjoining the paint plant. Executive and general offices occupy the entire first floor; on the second floor are production department offices, the analytical and production control laboratories, sample retaining room, laboratory grinding room, and several research and development laboratories.

Dibasic Acids and Polyhydric Alcohols Are Essential Raw Materials for Resins

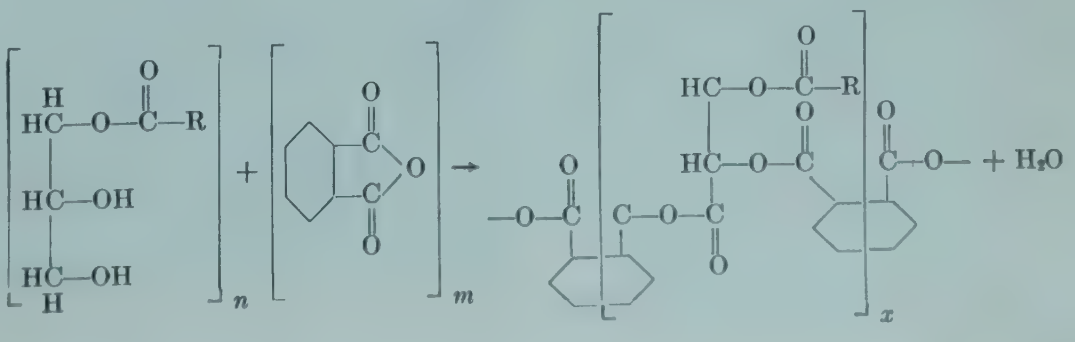
Theoretically any organic acid and alcohol might have value in the manufacture of alkyd resins, although relatively few of the economical ones have the necessary physical and chemical properties (*11*). DeSoto uses most of the common acids and anhydrides consumed by the paint industry, such as adipic acid, benzoic acid, fumaric acid, phthalic acid and some of its isomers (terephthalic acid and isophthalic acid), phthalic anhydride, and maleic anhydride. In the alcohol group, the plant consumes principally glycerol, pentaerythritol, ethylene glycol, and propylene glycol. DeSoto can, as the need arises, also use other raw materials: maleic acid, succinic acid and succinic anhydride, other isomers of phthalic acid (tetrahydrophthalic acid and hexahydrophthalic acid), sorbitol, mannitol, diethylene glycol, and 2,3-butylene glycol.

The most common example of alkyd resins is a compound derived from the reaction between linseed oil, glycerol, and phthalic anhydride. As such, phthalic anhydride is insoluble in linseed oil as well as most drying and semidrying oils. Since it is soluble in monoglycerides, the paint industry uses alcoholysis to great advantage.

Glycerol will react with drying, semidrying, or nondrying oils (and polyhydric alcohols) to form monoglycerides. Two moles of glycerol, for example, can unite with one mole of linseed oil to form sufficient monoglycerides for complete solution of phthalic anhydride, by the following reaction mechanism:



In practice the process also produces diglycerides, and leaves some unreacted glycerol and triglyceride in the final mixture. The monoglycerides (and diglycerides) react freely with acid components, such as phthalic anhydride, to form a resin in the second step of alkyd preparation:



From stoichiometric considerations, two moles of glycerol theoretically are required for every three moles of phthalic anhydride added later on. In actual practice, however, about $2^1/_2$ moles of glycerol usually produce better resins than a higher or lower ratio, within practical limits (*11*).

Polyhydric alcohols having four primary hydroxyl groups, such as pentaerythritol, can be substituted for glycerol. In this reaction, two molecules of phthalic anhydride are theoretically required for one molecule of pentaerythritol. A slight excess (10%) of the alcohol gives satisfactory products which also form large cross-linked molecules; water is a by-product of the reaction.

Pentaerythritol, having four primary hydroxyl groups and a symmetrical structure, gives greater probability of cross linkage than glycerol. Its products have many characteristics that are more desirable than the straight glycerol product and some that are not so desirable. They may have faster and harder air-dry properties at longer oil lengths, better gloss, and better chemical and water resistance. By contrast they may show poorer can stability and some evidence of seeding; pentaerythritol can be difficult to control color-wise during manufacture and has a higher cost per hydroxyl equivalent (*7*).

If a compound having only two hydroxyl groups, such as ethylene glycol, is employed instead of glycerol, then only one molecule of phthalic anhydride is required for each alcohol molecule. No cross linkage occurs with bifunctional reactants, only linear polyesters and water are formed.

Modified alkyd resins based on alcoholized oil use such raw materials as linseed, soybean, cottonseed, tung, fish, and dehydrated castor oils. With raw castor oil there is no need for the alcoholysis step, since phthalic anhydride, alcohol, and castor oil react directly under the conditions of esterification to form the alkyd (phthalic anhydride is soluble in raw castor oil).

Catalysts are desirable for the alcoholysis, although the reaction can be conducted satisfactorily at higher temperatures—between 525° and 550° F. without catalyst. In this range it is necessary to use a condenser on the reaction vessel to prevent loss of ingredients. Some of the more common catalysts include oxides of lead, calcium, barium, and zinc; hydroxides of calcium, sodium, and barium; naphthenates of lead, calcium, sodium, zinc, barium, lithium, and cerium; and resinates of lead, zinc, calcium, and barium. With the use of one of these catalysts, the reaction temperature can be lowered considerably—between 450° and 480° F. Even lower temperatures have been used, but this often extends the time required for monoglyceride formation to a point where it is impractical for economic reasons.

Alcoholysis is a critical step in the manufacture of resins; lack of uniformity in the amount of monoglycerides present affects later alkyd processing, the viscosity of the final product, and the resin's other physical characteristics. Poor gloss, poor stability, and impaired film appearance have been traced to irregularities in the alcoholysis product.

Glycerol is still the most widely used polyhydric alcohol (*7*) and probably retains its position because it naturally occurs in drying oils and can be used directly in alcoholysis. When it is in the competitive price range, glycerol is somewhat more economical since it contains the highest amount by weight of active hydroxyl groups. It can be employed to produce very long or very short alkyds and therefore gives greater manufacturing flexibility. The fact that it has been used for a much longer time and has a much larger background of technical information concerning its performance in finished products, naturally stands in its favor.

Resin Plant Serves Dual Purpose

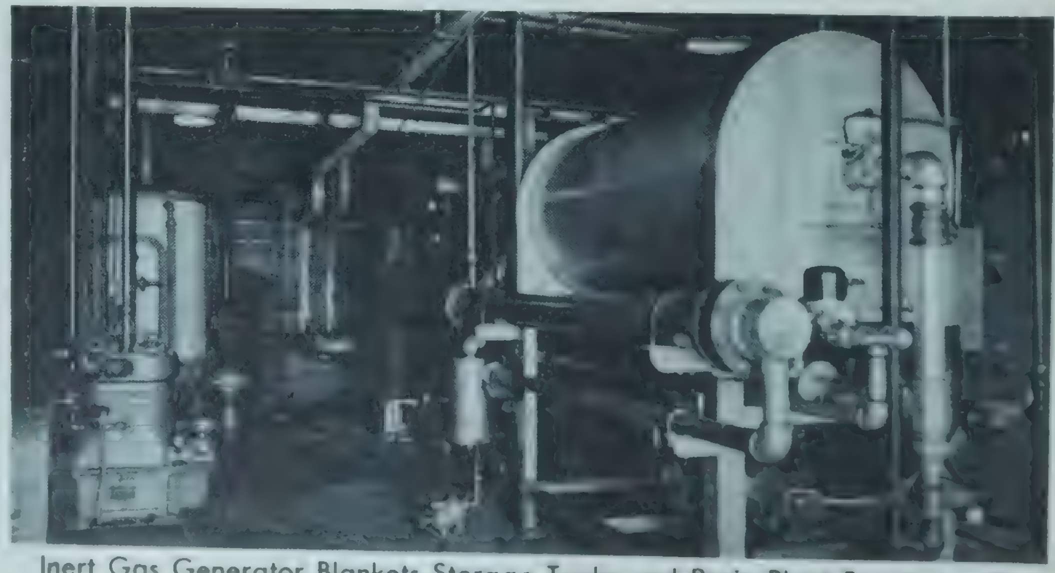
The resin plant, designed to serve a dual purpose, manufactures vehicles for the paint factory and for sale to other paint manufacturers, and also produces other type materials such as plastics, adhesives, chemical resistant finishes, and specialty products for sale to the petroleum, chemical, and food industries. Its products include bodied oils, all types of alkyd resins, emulsion or water dispersible vehicles, and numerous varnishes.

Equipment in the resin plant consists principally of two reaction vessels, 250- and 2500-gallon capacities, with auxiliary solvent recovery facilities, as shown in Figures 1 and 2. The smaller of the two vessels is used as a pilot or small batch unit, the larger for main production requirements. These units are capable of turning out 2,000,000 gallons of vehicles per year.

DeSoto's reactors, like most standard equipment for processing alkyd resins, are stainless steel. Considering the pale color of the product, ability to be cleaned with caustic soda, and service life of the equipment, stainless steel has a distinct advantage. Both reactors are heated by an indirect radiant gas fire of new design (*10E*), quite different from many of the Dowtherm systems employed in numerous other plants. Firing of these units is totally automatic and is operated by remote recording controls. All other equipment in the plant was designed by the engineering staff of the parent company.

The kettles operate at all pressures from 75 pounds per square inch gage to $^1/_4$ inch of mercury absolute, giving maximum flexibility. The inert gas generating system (*8E*) purges and blankets both reactors; steam ejectors provide the vacuum. DeSoto's condensing system returns solvent to the reactors with a solvent decanter, allowing for drawoff of the water layer containing soluble reaction by-products. Representative of the latest design in fume disposal facilities, DeSoto's auxiliary equipment (Figure 2) includes an oil-solvent prescrubber followed by jet contactors and a water spray tower.

All solid raw materials are conveyed from a central location into the vessel by an induced flow conveyor (*9E*), which is designed to prevent any contamination. Solids are weighed on a scale and charged by hand through an opening in the floor grating at ground level into an ice crusher (*13E*) connected to the base of the conveyor system. Liquid raw materials are moved through pumps and pipelines controlled from the process area, although the storage tanks and pump room are located some distance from the plant. The correct amounts of liquids are measured by a weigh tank (*11E*).



Inert Gas Generator Blankets Storage Tanks and Resin Plant Reactors with 80% N–20% CO_2 Atmosphere

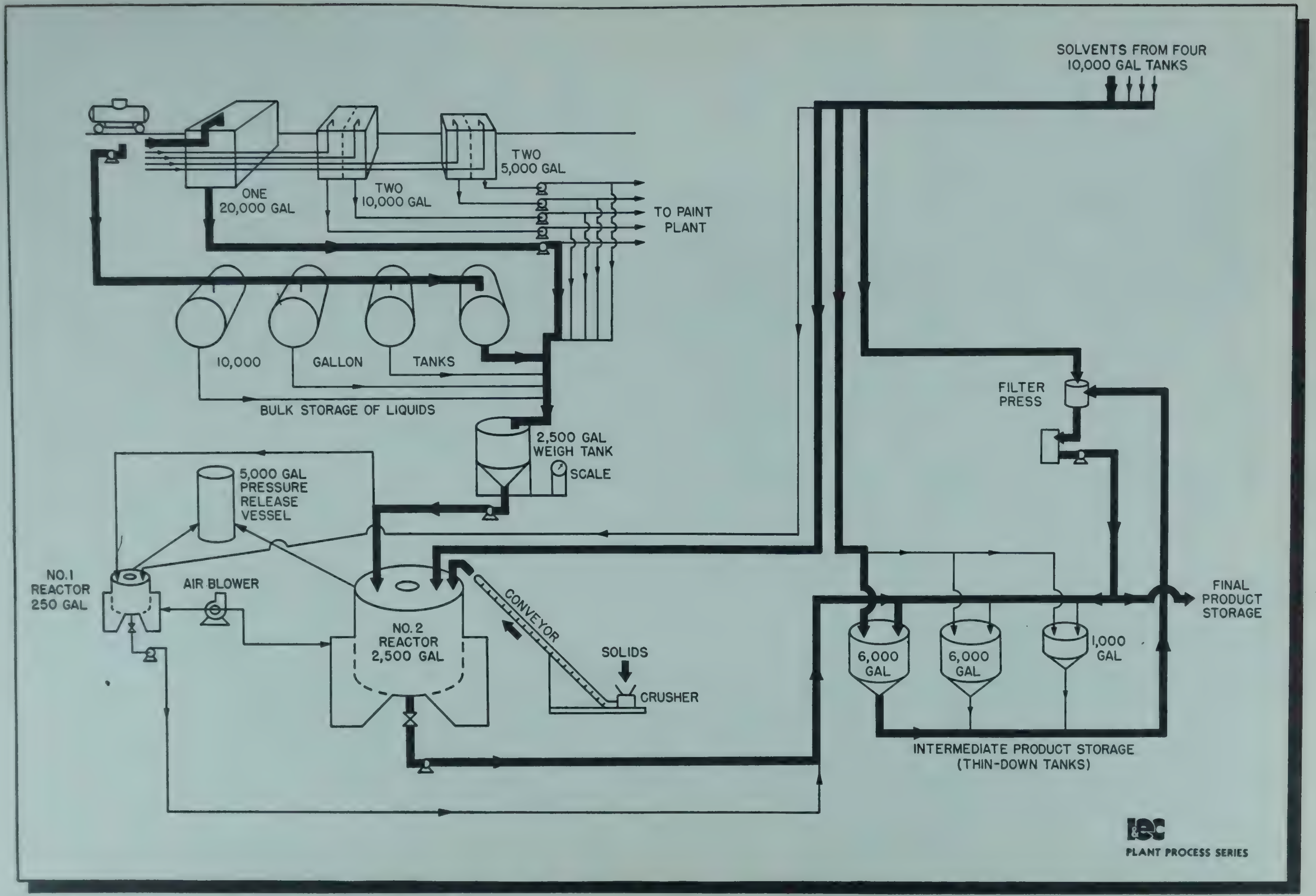

SOLVENTS FROM FOUR
10,000 GAL TANKS
ONE
20,000 GAL
TWO
10,000 GAL
TWO
5,000 GAL
TO PAINT
PLANT
10,000
GALLON
TANKS
BULK STORAGE OF LIQUIDS
2,500 GAL
WEIGH TANK
SCALE
5,000 GAL
PRESSURE
RELEASE
VESSEL
NO.1
REACTOR
250 GAL
AIR BLOWER
NO.2
REACTOR
2,500 GAL
CONVEYOR
SOLIDS
CRUSHER
FILTER
PRESS
FINAL
PRODUCT
STORAGE
6,000
GAL
6,000
GAL
1,000
GAL
INTERMEDIATE PRODUCT STORAGE
(THIN-DOWN TANKS)
I&EC
PLANT PROCESS SERIES

Figure 1. Flow Sheet for Production of Resin and Varnish at DeSoto Paint & Varnish Co., Garland, Tex.

To start off a batch of alkyd resins, the operator first charges the vessel with oil and glycerol (or other alcohol) and adds the required amount of catalyst by hand. (With the small reactor, everything is hand charged.) A typical formulation is given in Table II.

Controls are then set for a maximum temperature which may range from 400° to 480° F. The burners are actuated by an interlock system which requires that the inert gas line pressure be at a minimum of 25 pounds per square inch gage, cooling water be flowing to the water-jacketed burners, natural gas be up to the required delivery pressure, and the air blowers be delivering pressure to the gas burners. Until these conditions exist the burners are inoperative.

After the liquid agitator has been started and the kettle purged with inert gas, the burner ignition switch is closed. All eight burners of the large reactor (four on the small vessel) are automatically purged with air for 2 minutes. Both pilot lights are started to ignite the two primary burners, which in turn ignite the other six burners. (One primary burner ignites three secondary burners on the pilot units.) A flame rod inside the pilot light generates an electric current flowing in series; unless the circuit is closed signifying operation of both pilot lights, gas cannot be admitted to the primary burners.

The temperature recorder and controller has both a set point and an "overtemperature" control. If during production of a batch, the temperature should overshoot, all burners are automatically shut off, and cooling water is admitted at four times the normal flow. Both reactors cool at the rate of about 7° F. per minute.

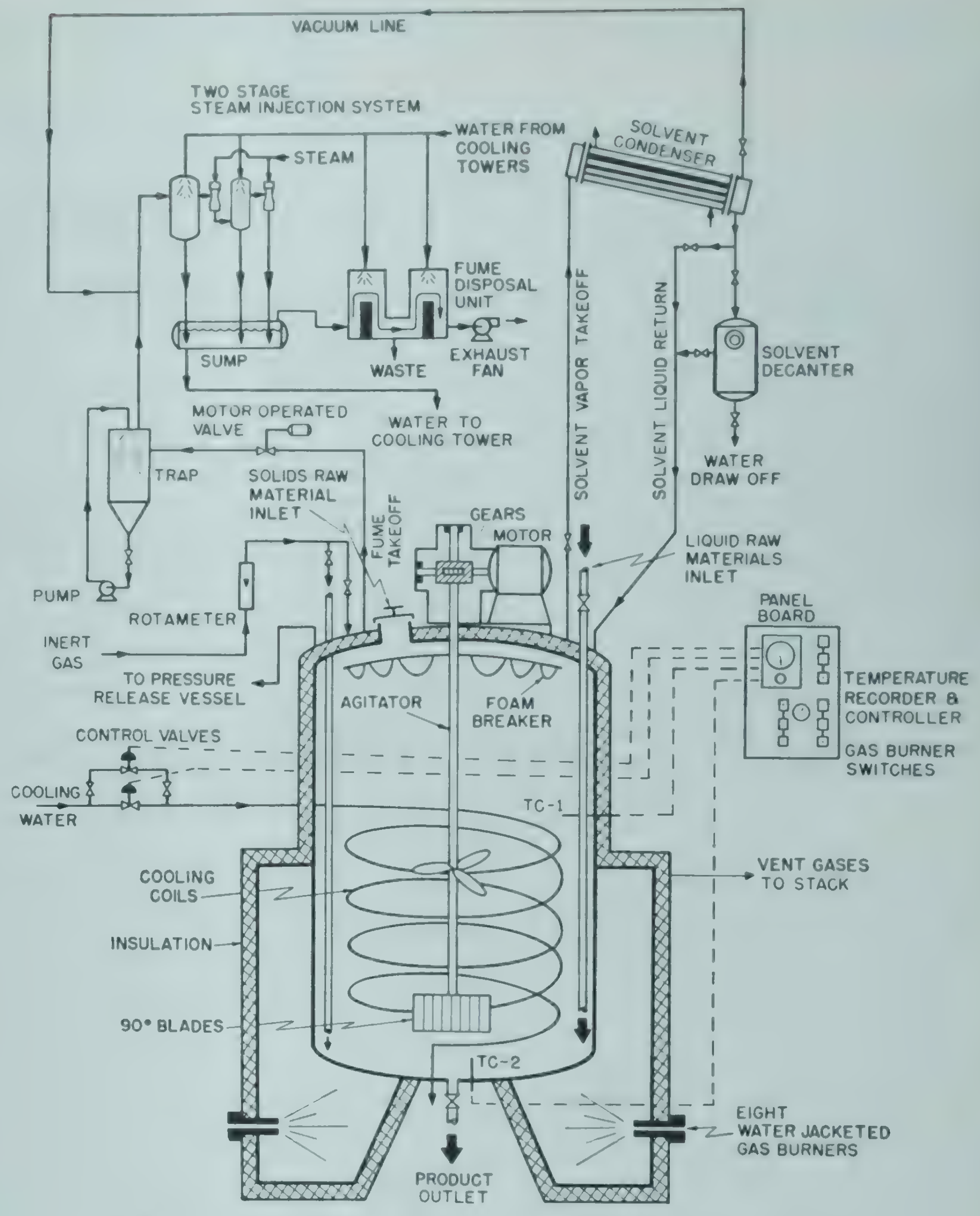

VACUUM LINE
TWO STAGE STEAM INJECTION SYSTEM
STEAM
WATER FROM COOLING TOWERS
SOLVENT CONDENSER
FUME DISPOSAL UNIT
SUMP
WASTE
EXHAUST FAN
SOLVENT VAPOR TAKEOFF
SOLVENT LIQUID RETURN
SOLVENT DECANTER
WATER DRAW OFF
MOTOR OPERATED VALVE
WATER TO COOLING TOWER
TRAP
SOLIDS RAW MATERIAL INLET
FUME TAKEOFF
GEARS
MOTOR
LIQUID RAW MATERIALS INLET
PUMP
ROTAMETER
PANEL BOARD
INERT GAS
TO PRESSURE RELEASE VESSEL
AGITATOR
FOAM BREAKER
TEMPERATURE RECORDER & CONTROLLER
CONTROL VALVES
GAS BURNER SWITCHES
COOLING WATER
TC-1
COOLING COILS
VENT GASES TO STACK
INSULATION
90° BLADES
TC-2
EIGHT WATER JACKETED GAS BURNERS
PRODUCT OUTLET

Figure 2. Resin Plant Reactor and Solvent Recovery System

Average Resin Processing Requires Eight Hours

Under normal conditions the large reactor reaches top operating temperature after 2 hours, progressing at a rate of 3.5° F. per minute. The small reactor reaches full heat in a shorter period, 1.5 hours, increasing at the rate of 5° F. per minute. Cooling coils within the reactor prevent overshooting; cooling water flow is controlled by the temperature recorder. As an added precaution six burners on the large reactor (three on the small one) are throttled back from 100% to 30% of fire and automatically shut off as the desired temperature is reached. The remaining burners operate between 30% and 100% of full fire as required, or may be automatically shut off during exothermic reaction.

Total processing time may vary between 3.5 and 10 hours; average batches run about 8 hours. Depending on the formulation, full heat can range from 400° to 600° F. and on occasion run as low as 225° F.

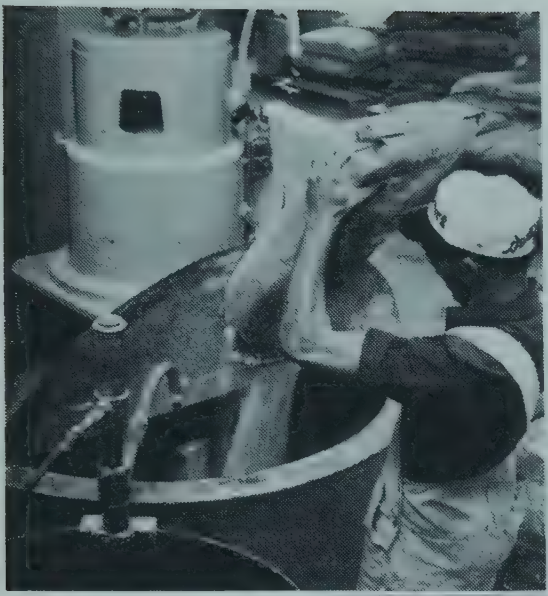
As the kettle hits top temperature, samples are withdrawn to determine the extent of reaction. When the desired amount of monoglyceride has been formed, three parts of methanol is soluble in one part of sample, which is checked in the laboratory (methanol solubility increases with monoglyceride concentration). Under normal conditions solubility may result immediately at full heat or occur after a 15-minute cook. If a satisfactory test does not occur in 15 minutes, the batch usually has been improperly prepared, and special treatment is required to salvage it. The batch is in bad shape if, for example, the glycerol dehydrates to form excessive quantities of diglyceride.

Table II. Typical Alkyd Resin Formulation (*11*)

(Not including catalyst)

	Per Cent
Alcoholysis	
Linseed oil	48.2
Glycerol	12.0
Resin processing	
Phthalic anhydride	35.7
Glycerol	4.1

At this point the normal batch is cooled to 300° to 400° F., and a color stabilizer, such as triphenyl phosphite is added. This compound improves the color of products that are easily oxidized during processing at elevated temperatures (400° to 540° F.) because of the presence of free peroxides and insoluble



One of 16 paint mixers on third floor that prepare pigments and vehicles for grinding in roller and high speed stone mills

Small batches of pigments and vehicles are mixed in a pony mixer (third floor); batches are transferred to roller and high speed stone mills by a compressed air hoist

Plant's 1000-gallon pebble mill, "Big Bertha," is suspended from second floor ceiling; mill weighs 104,000 pounds fully loaded

Paint Production

iron salts. Triphenyl phosphite will dissolve the calcium phthalate precipitate found in alkyd resins when calcium hydroxide is used as the catalyst for alcoholysis. Its presence will also catalyze certain types of esterification and will retard color formation at room temperature of orange shellac during storage in tin cans. Too much triphenyl phosphite must be avoided, as it acts as an antioxidant and can retard the air drying of films (*11*).

Phthalic anhydride or dibasic acids are then added, and the reaction mixture is heated between 400° and 500° F. for a period of 2 to 6 hours. During this period the monoglycerides are converted to the polyesters by esterification. Samples are again checked by the laboratory; acidity indicates the extent of reaction. Viscosity of the resin is also measured in an appropriate solvent such as mineral spirits, xylene, or others. Color is checked by a colorimeter for conformance to established consumer acceptance.

More than 98% conversion is needed to eliminate product contamination by raw materials. In the majority of cases this degree of completion is also required to give the final product its favored chemical and physical properties. During the final reaction stages, plots are constructed of the physical and chemical properties of the batch for extrapolation to determine approximate completion time. A semilog plot of viscosity versus time gives a straight line, whereas acidity gives a parabolic curve.

After essential completion of the reaction, the operator cools the batch to a temperature below the boiling point of the solvent to be added. Solvents are pumped into the kettle and further cooling takes place. The reaction mixture is transferred to thin-down tanks with additional solvent added for flushing down the reactor; there it is held in intermediate storage. Final amounts of solvents and other agents are added in the thin-down tanks prior to final product testing. At this stage the laboratory checks such end-use properties as density, air-drying characteristics, heat-curing characteristics, emulsifiability, compatibility with other resins, and chemical resistance.

When the material has passed this initial inspection, the resin is filtered in a totally enclosed horizontal plate filter (*3E*). The Garland plant uses diatomaceous earth as a filter aid in combination with filter paper. Cloths are difficult to clean because many of the solutions air dry; paper can be economically discarded. Solid impurities (inerts from the raw materials) are removed, and the final solution is checked prior to shipment for such properties as viscosity, acidity, solvent content, and specific gravity. The final product is charged into 55-gallon drums or goes to tank storage. Material from the storage tanks is either used by the paint plant or sold in drum or tank car quantities.

Turbine-type Agitators Give Best Results

Agitation is an important factor in alcoholysis and resin processing, since some ingredients are immiscible, and turbulence increases reaction rates. Although agitation may be furnished by propellers, paddles, or a turbine, the turbine-type agitators give best results (*11*). DeSoto uses three-bladed propellers connected to the center of the agitator shaft, with the turbine-type blade at the bottom.

When preparing alkyd resins, agitation should be started as soon as the constituents are liquefied and continued until the product is ready for thinning. For optimum mixing conditions, a turbine diameter not less than one third of the vessel diameter is recommended, with peripheral speeds in the range of 600 feet per minute (*11*). DeSoto's agitator is driven by a two-speed motor with changeable gear ratios to permit shaft speeds from 50 to 200 r.p.m. (*14E*). New equipment may be tested with a known formulation under carefully controlled conditions (comparing reaction times with a standard) to determine if agitation is sufficient.

During alkyd preparation, inert gas is bubbled through the reaction mixture to improve agitation, to promote better color, and to increase the reaction rate by removing water of esterification. Color formation during processing is generally attributed to oxidation; blanketing with inert gas minimizes this effect. Carbon dioxide and nitrogen have been studied for this use and similar results are obtained with either gas. In using an inert gas, the quantity and degree of dispersion are the most important factors.

Inert gas flow must be started at the beginning of heating during alcoholysis and continued until the batch is finished including thinning. For best results the gas should be introduced into the alcohol layer or close to the kettle bottom (common practice at Garland) and preferably through fine openings in tubes or other diffusing devices. To ensure complete drainage, all openings are placed on the underside of the gas disperser.

The inert gas system at Garland blankets both reactors; it is used everywhere in the resin plant to supply units that normally would require compressed air (instruments, pneumatic hoists, and the sampling system).

Varnish Production Requires Careful Control

Large-batch, closed-kettle varnish production can be a tricky operation without proper instrumentation and adequate cooling, simply because certain types of reactions are highly exothermic. Incomplete removal of used raw materials and by-products is also a problem. DeSoto overcomes the latter difficulty by use of vacuum, and inert gas, and agitation.

Varnishes generally consist of three components—an oil, a hard resin, and the solvent. Many formulations use linseed, dehydrated castor, China wood oil, or other unsaturated oils. The hard resin may be a petroleum resin, natural resin, esterified rosin, phenolformaldehyde, modified phenolformaldehyde, or some combination of these. Numerous solvents perform satisfactorily; mineral spirits is a popular component. Other materials for varnish manufacture have been described by Shearon (*16*).

One of the typical formulations used at Garland contains 100 pounds of phenolic resin, 12.5 gallons of linseed oil, and 12.5 gallons of China wood oil—enough material to produce 25 gallons of long spar varnish. "Long" and "short" are terms used in the paint industry to designate oil to resin ratio (gallons of oil per 100 pounds of resin). As a general measure short varnishes vary from 2 gallons to 12 gallons, medium varnishes from 12 to 40 gallons; anything over 40 gallons is a long varnish. In terms of physical properties, the shorter varnishes produce a more brittle film, although flexibility depends to some extent upon the type of oil and resin in the formulation.

In running off a typical varnish batch, the operator charges hard resin and linseed oil into the reaction vessel and sets the temperature controls at 560° F. The mixture is held at top temperature for 15 to 20 minutes until it acquires the desired viscosity. China wood oil is added, the mixture reheated to 465° F., and held there for another 15 minutes for a second viscosity check.

Before addition of solvent (mineral spirits), the batch must be cooled below the solvent's boiling point (around 400° F.). After this phase, the operator transfers the reaction mixture into thin-down tanks, where dryers are added at a temperature below 250° F. Best results are obtained at 200° F.; suitable drying agents such as naphthenates or fatty acid salts of lead and cobalt may be employed (*16*). Filtering is the final step in the operation.

Formulation of varnishes must follow a definite sequence to produce a desirable product. China wood oil is added during the final cooking phase because it polymerizes considerably faster than linseed oil. Whereas linseed oil may be held at elevated temperatures for many hours before gaining appreciable viscosity, China wood oil would form very high molecular weight polymers, in some instances insoluble ones. (China wood oil held at 540° F. for 12 minutes will produce a rubberlike mass.)

As might be expected, there are many variations in the formula for tailoring products. Varnish consisting entirely of China wood oil and phenolic resin, for example, has increased alkali resistance, faster drying properties, and a tougher and more flexible film.

Gravity-Flow Large-Batch Paint Operation Proves Most Economical

Actual paint manufacturing (Figure 3) begins on the paint plant's third floor, where solid raw materials are blended with liquids drawn from lines leading from the tank farm. Liquids from the storage area are pumped up to the third floor; coded bags of dry pigments arrive from the receiving department via a 12,000-pound capacity automatic elevator. Up to 140 tons of pigment bags can be stored on pallets, along with a lesser quantity of liquids in drums. During the mixing and subsequent operations, formula cards indicate by code number the various pigments and vehicles required in each batch. All liquids are weighed into change tanks, as specified, on 6000-pound scales (*19E*). All materials, including liquids, are added by accurate weight rather than volumetrically.

Some of the basic blends are prepared in 16 paste mixers (*6E*) having three blades set at a slight angle to the shaft. Each mixer (160-gallon charge capacity) is driven by a $7^1/_2$-hp. motor. Operators charge pigments by hand from full bags or weigh out smaller amounts. From the change tanks vehicles are transferred into the mixers by air-driven pumps immersed below the liquid surface. Located on the roof of the building, a 20-hp. fan draws dust from the mixers into a cloth screen dust collector (*16E*).

To ensure good mixing DeSoto charges pigments simultaneously with the vehicles, thereby reducing mixing time; only 15 to 45 minutes is required. Processing is further expedited after mixing has been completed, by dropping the "batch" cards through detachable chutes to the mill floor below. Two pony mixers (*5E*) on the third floor operate in a similar fashion for processing small batches in 15- and 50-gallon tubs. Whereas the paste mixers are connected by pipelines to high speed stone mills and by chutes to roller mills on the second floor, the pony buckets must be transferred by elevator using air-operated chain hoists for loading and unloading.

Materials from the third floor flow by gravity down to the mill room for processing in four high speed three-roll mills (*12E*) and four high speed stone mills (*15E*). Mill operators control the release of liquids from the mixers by means of gate valves, on receipt of the batch tickets from the mixer operators. Each of the three-roll mills is driven by a 45-hp. motor, geared for two different speeds. Each stone mill is powered by a 20-hp. motor. During a small batch run, these mills discharge into 100- and 200-gallon change tanks, which may also be used for rerunning a particular batch. Normally the base grind flows by gravity into 1000- and 2000-gallon thin-down tanks mounted flush with the floor. Here the bulk of the reducing material is added, and the batch is shaded and adjusted. Roller mills are employed especially for grinding fine enamels; the high speed stone mills process house paint and flat wall paint.

According to the type of paint produced, DeSoto also uses three pebble mills and five steel ball mills (*17E*), which are charged through openings in the third floor. The pebble and ball mill operators perform both the charging and grinding operations. The pebble mills accommodate 100-, 250-, or 1000-gallon charges; two of the small steel ball mills hold 50 gallons, and the larger ones have a 250-gallon capacity. Total capacity of the ball and pebble mills exceeds 2200 gallons. Although some plants have supported ball mills near the ceiling on separate foundations for

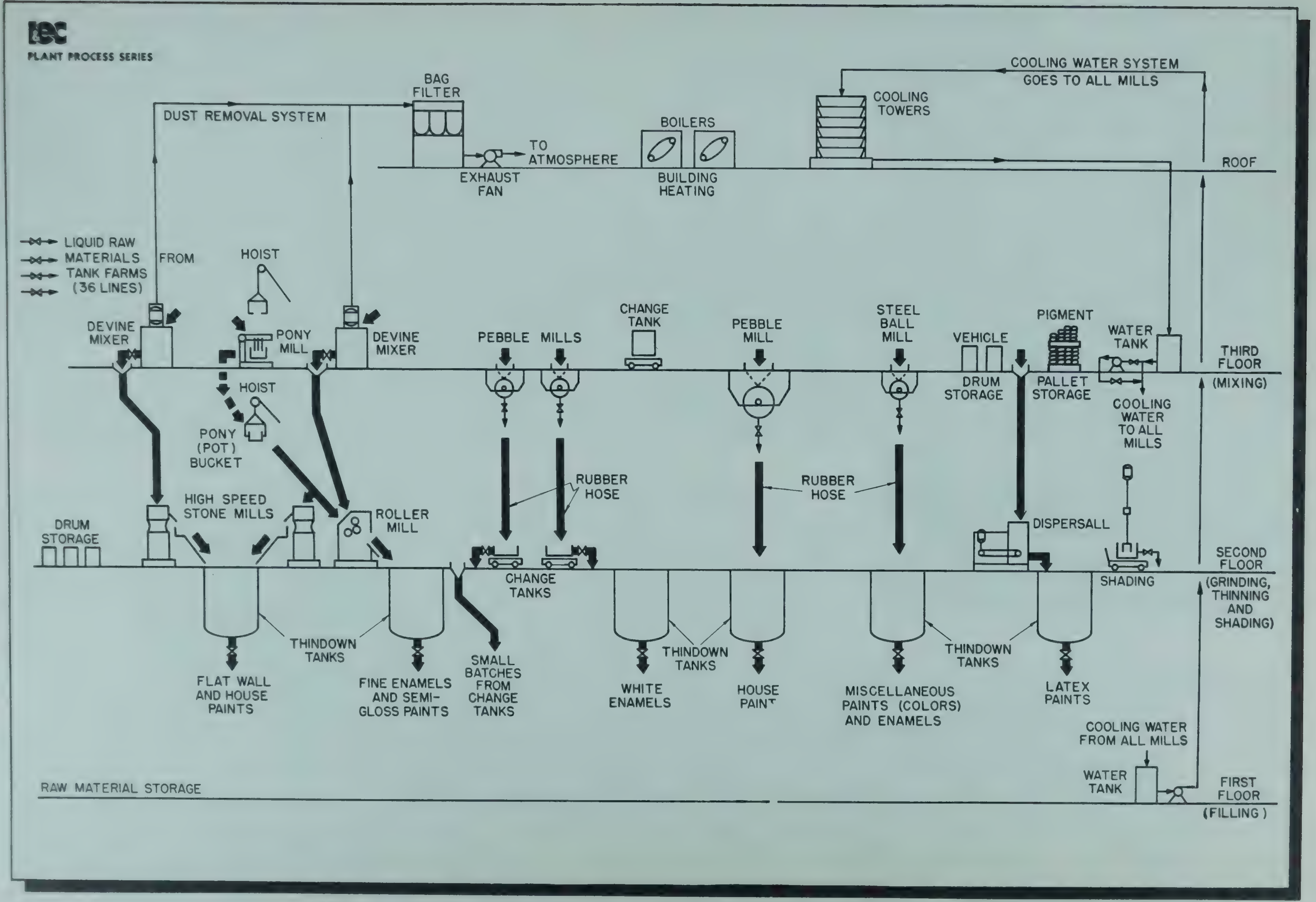
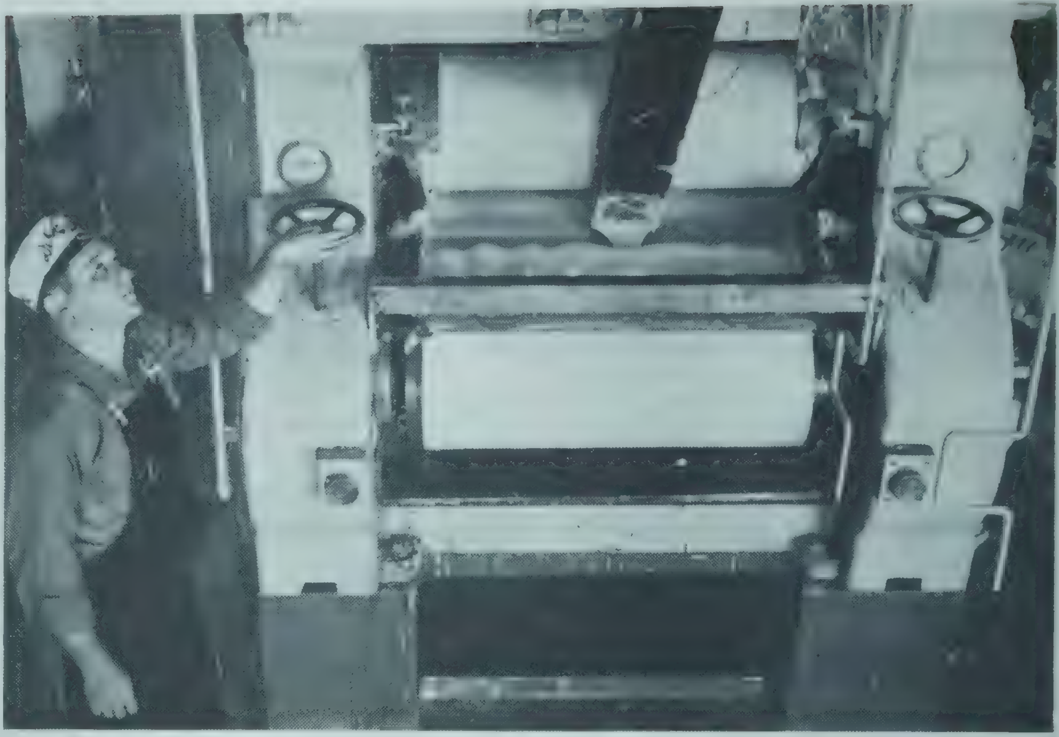

I&EC
PLANT PROCESS SERIES
DUST REMOVAL SYSTEM
BAG FILTER
EXHAUST FAN
TO ATMOSPHERE
BOILERS
BUILDING HEATING
COOLING TOWERS
COOLING WATER SYSTEM GOES TO ALL MILLS
ROOF
LIQUID RAW MATERIALS FROM TANK FARMS (36 LINES)
HOIST
DEVINE MIXER
PONY MILL
DEVINE MIXER
HOIST
PONY (POT) BUCKET
PEBBLE MILLS
CHANGE TANK
PEBBLE MILL
STEEL BALL MILL
VEHICLE
DRUM STORAGE
PIGMENT
PALLET STORAGE
WATER TANK
COOLING WATER TO ALL MILLS
THIRD FLOOR (MIXING)
DRUM STORAGE
HIGH SPEED STONE MILLS
ROLLER MILL
RUBBER HOSE
RUBBER HOSE
CHANGE TANKS
DISPERSALL
SHADING
SECOND FLOOR (GRINDING, THINNING AND SHADING)
THINDOWN TANKS
FLAT WALL AND HOUSE PAINTS
FINE ENAMELS AND SEMI-GLOSS PAINTS
SMALL BATCHES FROM CHANGE TANKS
WHITE ENAMELS
THINDOWN TANKS
HOUSE PAINT
MISCELLANEOUS PAINTS (COLORS) AND ENAMELS
THINDOWN TANKS
LATEX PAINTS
COOLING WATER FROM ALL MILLS
WATER TANK
FIRST FLOOR (FILLING)
RAW MATERIAL STORAGE

Figure 3. Flow Sheet of Paint Production at DeSoto Paint & Varnish Co., Garland, Tex.

many years, DeSoto was among the first to bolt its mills to I-beams on the second floor ceiling, thus adding to convenience in use, eliminating cumbersome supports, and freeing additional floor area. Rubber mounts reduce vibration to a minimum.

The largest pebble mill, "Big Bertha," having a 1000-gallon capacity, contains 16,800 pounds of pebbles and weighs 104,000 pounds fully loaded. All the pebble and ball mills run for approximately 16 hours during a normal processing period, although in isolated cases greater grinding times have been required. All mill schedules are set to allow for a complete cycle of loading, grinding, and unloading in 24 hours. All the mills are water-cooled to a constant temperature during operation. When the grinding is completed, operators empty the mills into thin-down tanks through a neoprene hose. Here one of the principal advantages of ceiling suspension becomes apparent. The neoprene hose permits easy accessibility to any one of six thin-down tanks. By using an extension hose, operators can reach any tank on the floor.



High Speed Roller Mill

These mills (on second floor) have three rolls, each rotating at a different speed; mills are particularly used for grinding fine enamels

DeSoto processes latex paints in units separate from its regular equipment. Raw materials from the latex storage tank are pumped through stainless steel lines to the third floor, where they are weighed in stainless steel change tanks, and dumped through a chute into a mixer (*1E*) on the second floor. Similar in action to a juice blender, the Dispersall mixer holds 220 gallons and is stainless steel–lined for protection against corrosion. This unit discharges into a 1000-gallon thin-down tank, Heresite lined.

Off to one side of the mill area, operators match colors to various permanent standards. At this point, prior to filling operations, all batches must be approved by the laboratory as to color, viscosity, density, and other specifications. Shading mixers are equipped with detachable agitator blades, so that the drive may be utilized for other batches, pending approval of laboratory samples. The agitator blades are left in the portable shading tanks during the check, in case further shading is required. In most paint plants, the agitator blades remain with the drive, and only the shading tanks are portable.

When approved, batches are drained from the twenty-four 1000-gallon and the four 2000-gallon thin-down tanks into filling machines on the first floor. All tanks, suspended from the second floor, have round corners and sloping bottoms to give better agitation of the material and better drainage. Large openings are provided at tank tops to facilitate cleaning.

DeSoto uses automatic filling and labeling machines (*2E*, *7E*), although some small batches are filled by hand. This equipment can move directly under the thin-down tanks for tandem filling, labeling, and packaging in cartons. From the portable filling machines cartons are transferred by old type gravity conveyors (brought to Garland from the Memphis plant) into the storage or finished goods warehouse. The conveying units are not permanent equipment; DeSoto is now studying a number of power conveying systems for a permanent installation.

Desoto Maintains Effective Planning and Production Scheduling

Paint production is only one step of the over-all operations, but a very vital phase which must intermesh smoothly with purchasing, formulation, sales, accounting, inventory, capital investment, budgetary control, personnel management, advertising and promotion, and managerial acumen, to make a successful, profitable business (*12*). The accomplishments of production planning and scheduling are, as expected, beset with many pitfalls. Generally speaking, production planning is a "concept" that must be tailored to fit the needs of a particular company.

Production planning and scheduling may be defined as listing in advance the batches to be run on each piece of major equipment and the estimation of expected starting and finishing time (*13*). It aids in maintaining adequate inventory of active raw materials, without overstocking, and permits attainment of delivery committments. Efficient scheduling paves the way for finished product inventory controls within the limits of available warehouse space and monetary tie-up. If practiced effectively, it helps level peaks and slumps in production, especially during surges of short-delivery orders.

Many of the larger plants use a scheduling board (*13*); DeSoto has one of its own design. The idea for this particular type of board originated with DeSoto 5 years ago in Memphis and has grown through five versions from a 3 × 4 foot model to its present size, 8 × 16 feet. The production department attempts to schedule shelf goods rather rigidly since needs here can be predicted on a seasonal basis, proved by past performance; industrial sales are more individual in nature, and production here is scheduled on a more flexible basis. When starting out to plan for production, the plant superintendent, schedule clerk, and both the mixing and grinding foremen hold a meeting just before closing time to discuss operations for the next day. At this meeting they have a report from the tabulation department regarding warehouse inventories. Also at their disposal is a sales department projection on what the company expects to sell in the ensuing 60 to 90 days, enabling the warehouse to operate on a 30-day finished goods inventory.

After studying the industrial orders on hand, this group prepares production tickets which are placed on the board under the mixers or grinding mills scheduled for operation. Batch tickets based on production tickets are available to operators at the start of the next morning shift. All batch cards are in four-part form—mixing and grinding, filling, labeling, and inventory. When a batch has been mixed, the fourth section of the ticket goes to the inventory control department, for credit to raw materials. Other sections of the batch cards go out to the indicated depart-

Paints and Enamels Are Thinned in 1000- and 2000-Gallon Tanks Mounted Flush with Second Floor

ments, notifying them to prepare for processing. Batch tickets returning from the various departments are used to record quality control tests and finished goods inventory credits.

Meanwhile, production tickets are transferred on the scheduling board to show in which piece of equipment the batch is being processed. This procedure enables the superintendent to watch the progress of all batches at all times. Production tickets also have certain other important information recorded—date, quantity of batch in gallons, catalog number, and the quantity of finished goods (number and size of cans). Different colors are used to designate different destinations.

A glance at the schedule board immediately reveals whether a particular batch is in the mixing, grinding, thinning, or shading stage. Separate positions are provided when a batch is being tested in the laboratory and has been approved for filling; the final position on the board represents a filled batch. Each tank is numbered and provided with a card to indicate if it is empty, in use, or being cleaned. From these records, it is possible to establish "down time" of each piece of equipment, keeping check on overall efficiency and ensuring maximum utilization. If any batch is delayed for any reason, this fact is duly noted on the schedule board.

The production department keeps a record on the number of units (containers for shipping) scheduled and the number produced during the month. Entries three times a week from data gathered by the tabulating department show how many units are on orders being held, those shipped, and units open for sale.

A tabulating department, in conjunction with production scheduling, produces records for inventory control. This department, located in a soundproof room, develops information on all material movements. Remington Rand equipment (*18E*) includes a summary punch, two key punches, a tabulator, sorter, interpreter, and auxiliary equipment (two summary punch wiring units and five tabulator wiring units). In the future, DeSoto plans to add two more summary punches and two more tabulator wiring units.

Remington Rand cards have 45 columns, permitting simultaneous tabulation of six different items. For most reports the machines assemble data regarding catalog number, size, and quantity of the item produced. Through the use of cards of various colors, this department keeps a running inventory on trade sales finished goods, industrial finished goods, raw materials received, raw materials consumed, and the receipt and consumption of raw materials in the resin plant. Reports are current; when a report is turned out at 5:00 P.M., it contains all the shipments made on the previous working day, all production until noon of the report date, and all orders received in that day's mail.

Unit Buying Control Guide and Consolidated Shipments Facilitate Order Filling

Filling orders for a large distributor like Sears requires maximum coordination for maximum economy. Sears's stock is laid out in the warehouse to follow the "Unit Buying Control Guide"; order forms from all stores list items in the same sequence. In the warehouse, items are stored in this sequence for ease of filling orders. Order pickers go down one aisle and up the next, working directly from the requisition. This procedure eliminates recopying the requisition onto pickers' tickets, saving both time and labor. Orders are made up on pallets and placed in bays next to the wall for loading into trucks.

The importance of this operation is better understood in the light of DeSoto's production: some 1500 different items in seven sizes range from $^{1}/_{4}$-pint cans to 5-gallon cans and 55 gallon drums. Some materials are ring sealed to permit mailing (*4E*). DeSoto markets its own products in 13 states and serves Sears's retail outlets in three additional ones. Wherever possible, shipments are routed for consolidation of less-than-truckload lots, ensuring maximum use of trucks. This procedure permits shipment of orders in full truckload quantities by stopovers along the most direct route.

Efficiency Centers in Materials Handling System

Paint manufacturing economy at Garland centers largely around efficient handling of the large number of raw materials and finished products. Purchasing department records show that DeSoto uses some 427 different types of vehicles and pigments for the production of almost 1500 items.

The plant has more than 100,000 square feet of storage space, efficiently designed so that all materials proceed in one direction only (from raw materials to finished goods). Hydraulic dock ramps at the raw materials receiving platform can be raised or lowered to accommodate any height truck body; this eliminates lifting or the use of portable ramps. These rectangular steel platforms are built into the concrete dock with one end hinged flush with the floor. The end nearest the truck can be raised or lowered; when not in use the ramp remains flush with the dock floor. In the finished goods shipping department five of these devices load five trucks simultaneously.

In the past, relatively little scientific attention has been paid to solids handling in paint plants (*16*). Labor costs, however, have forced most manufacturers to use pallets for unloading, and some use semilive skids for finished product storage (*16*); DeSoto receives most of its solids in unit-load prepalletized form. Raw materials coming into the receiving department at Garland are either held there for storage or transferred by fork-lift trucks into an elevator and then up to the third floor of the paint plant for processing. Each pallet is normally loaded with about 2000 pounds of material.

Both tank cars and tank trucks are emptied in the unloading area through 2-inch lines. If necessary, four tank cars can be unloaded simultaneously; about 3 hours is required to unload a car. The transfer is made by pumps at the unloading station through a neoprene hose into headers of thirty-six 3-inch lines leading to the tank storage building.

This building contains 28 mild steel tanks, two with 20,000-gallon capacity, 26 with 10,000-gallon capacity. Eight of the 10,000-gallon tanks have connecting dividers for use at 5000 gallons or full capacity. Some of the earlier plants in this country employed manifolds, but the trend today is toward separate lines to eliminate contamination. At Garland each tank has a separate line that carries liquids either to the resin plant or to the second and third floors of the paint plant. All 36 lines pass through underground tunnels, which are becoming increasingly popular in modern plants.

DeSoto's tank farm is in a totally enclosed building for temperature control. Some plants such as that of Pittsburgh Plate Glass Co. (*8*) in Springdale, Pa., also considered a modern postwar operation, take advantage of similar techniques and house their liquids in the basement. For future expansion needs, space in the tank farm building at Garland has been allocated to accommodate 26 additional 10,000-gallon tanks, which if installed would give a total storage of 560,000 gallons.

In the storage areas, over 400 items are stocked, ranging from 1-gallon cans of liquid silicone costing $28, to an 8000-gallon tank car load of linseed oil valued at $12,000. Pigments in quantities of only a few pounds may cost as much as $11.45 a pound, if they are the phenylmercury type, whereas some whitings can be had for only a cent a pound in carload lots (exclusive of shipping charges). Freight on some of the cheapest pigments actually cost more than the material itself.

Adjacent to the tank storage room, a pump room containing 36 pumps, each having a capacity of 90 gallons per minute at 65 pounds per square inch pressure, feed the paint and resin plant. As pointed out by Freeman (*8*), large pumps are desirable for moving viscous liquids, and lines should have a diameter of 3 inches or more; DeSoto and Pittsburgh Plate Glass both use 3-inch lines in their new plants. All pumps in the Garland plant are electrically driven by $7^1/_2$-hp. motors.

In addition to roof storage on the second floor of the paint factory, DeSoto also uses the roof of the third floor to good advantage. The process water system, which cools the various mills in the paint factory, has a separate cooling tower apart from the ordinary water demand of the plant. This tower is located on the roof with two automatic low pressure (15 pounds per square inch gage) boilers. To place these 75-hp. boilers in the basement would have required digging through $2^1/_2$ to $6^1/_2$ feet of rock. Company engineers found they could save a $35,000 excavation cost and also use much shorter stacks by a roof installation.

Even though the tank farm has an explosionproof electrical system, an inert gas generating unit blankets the storage tanks for protection against oxidation and possible explosion. As an additional precaution, naphtha tanks in the tank farm are isolated by fire walls. Also equipped with a sprinkler system, both plants are ensured of adequate water at all times by a 100,000-gallon water tank.

The inert gas generating system (*8E*) burns natural gas to form an oxygen-free atmosphere; it is primarily a combustion unit and a dessicant drying unit which turns out 1000 cubic feet of gas per hour. The inert gas is stored at 80 to 85 pounds per square inch pressure in a 1000-cubic foot tank; similar systems have been described by Barstow (*3*) and by Funk (*9*).

Explosionproof electrical systems have been installed throughout processing areas in the paint and resin plants. The entire processing area of the resin plant, including the heating system for the kettles, is explosionproof. This includes everything from the lights in the ceiling to the floor itself, which is sparkproof. In order to save the cost of these systems where possible, the resin plant has a room for conventional electrical equipment (all that could be located outside the processing area), which is isolated from other sections of the plant by a fire wall.

Remote control of raw material pumps from the processing area of the paint factory has been standard practice for many years in well-designed plants (*8*). DeSoto has added another desirable feature for protection against leakage; switches automatically shut off the pumps before the valves completely close, depressurizing the lines. The switching system alone cost $30,000.

Well Equipped Laboratories Include Research Facilities

The paint plant's laboratories are probably as well equipped as any in the industry. All raw materials used for paint manufacture are bought to specifications and tested by the chemical laboratory before entering the process. Chemists in the production control laboratory check each batch before approval is given to perform the filling operation; all products are critically examined for proper consistency, ease of application, drying time, color, and gloss. This laboratory also performs periodic tests on retained samples. A well-equipped research and development laboratory has been provided for study of customer's problems.

The laboratories test paints for washability, wear, weathering, and many other properties. One of the many tests is that of applying flat wall paint to panels, which is allowed to dry and then scrubbed with soap and water. For routine tests the laboratories have a color comparator, viscometer, gloss meter, film thickness gage, and impact tester. Other equipment includes a cone roller, walk-in spray booth, ovens, salt spray and humidity cabinets, lithograph machine, and pH meter for latex paints. All indoor tests are complemented by outdoor exposure tests.

All types of finishes are exposed to alternate "rain" and "sunshine" conditions in a weatherometer—simulating as nearly as possible outdoor exposure. DeSoto's weatherometer "rains" by means of water sprays for 7 or 8 minutes out of every 2 hours' exposure. Sunshine is simulated with carbon arcs.

Samples of each batch retained in the laboratories for one year are frequently checked for viscosity, gloss, color, skinning, settling, and gelling. DeSoto does not hesitate to recall from dealer shelves all material from any batch that appears to be failing to hold up to established specifications for performance or shelf-stability.

Even the resin plant has its own laboratory that works very closely with sister companies and a central research laboratory in Chicago. Because many requests for products are local, research facilities have been established at Garland to give DeSoto's customers adequate service in connection with problems of a local nature.

Paint Industry Seems Unable to Stand Still

During World War II the military services consumed large volumes of paint, and this probably gave rise to the G. I. expression: "If it moves salute it, if it doesn't move paint it." No one can deny the great importance of paints to the war effort. However, the industry did not slump as a result of relaxed military requirements during the postwar period but went on to greater records of production.

Availability of new raw materials, new uses for paints, and the desire to improve quality have constantly exerted pressure on the formulator to change and add to his line of products. Postwar growth of the industry has been phenomenal; dollar volume of sales is up almost 60% since 1946. Part of this increase is undoubtedly due to the current "do it yourself" trend.

In recent years latex paints have sold more widely than any previous type of water-thinned paint. Latex paints are causing manufacturers of oil flat wall coatings considerable concern.

Numerous superior qualities have been claimed for latex paints, and promotional publicity has been exceedingly clever. How much of the consumer attraction may be attributed to the novelty of using a "rubber" paint is hard to evaluate. Among the most promising paints recently developed are those based on polyvinyl acetate, acrylics, and copolymers of styrene and butadiene. Polystyrene and vinylidene chloride are also showing considerable promise as raw materials.

In the pigment field considerable improvement has resulted from using jet-mill grinding methods, where the pigment size is regulated by the feed rate to the mill. Among the advantages cited are those of lowered oil absorption, easier wettability and dispersibility, and increased tinting strength. Since moisture can be eliminated, pigments will arrive at the plant dry, if packed in sealed plastic liners.

Synthetic resin consumption by the paint industry has been increasing for many years. Introduced during the last few years, styrenated alkyds are becoming more prominent as materials for low cost, fast-drying enamels, for baking undercoats, and for air-drying undercoats. Already the Armed Forces have recognized their importance, as shown by some of their new paint specifications based on these resins. Epoxy resins, which have grown from comparative obscurity in 1946 to an expected production of almost 30,000,000 pounds this year, have found wide usage. These resins, when esterified, are compatible with oils and other resins, are soluble in most solvents, and can be used in formulating air-drying and baked enamels.

Varnish making was the first utilization of polymerization and copolymerization processes, but recent developments have far surpassed the field of varnishes. Some of the new copolymers which have been introduced include such materials as styrene, butadiene, cyclopentadiene, acrylonitrile, vinyltoluene, and allyl alcohol. A bright future has been predicted for copolymers in general.

The use of paints to retard or prevent spreading of fire has attracted considerable interest. One of the main problems here is that of suitably testing the products; different materials vary widely as to their effectiveness, depending on the hazard to which they are exposed. More attention is being given to the development of anticorrosive, chemically resistant, heat resistant, and antifouling paints.

Methods of coating application are also getting their share of attention. Pressure-fed brushes and rollers have speeded application considerably. The latter is catching on with home users in the "do it yourself" program promoted by the building materials industry. One of the more fascinating developments is that of aerosol bomb dispensers, which have worked well for touch-up enamels and for clear coatings.

It is, of course, difficult to predict exactly what changes will take place in the next few years, although the general trend can be outlined. Much of the change in most paint factories during the past few decades has been necessitated by laboratory developments. Latices, epoxy resins, polyesters, amines, and other recent developments have created the need for new equipment and new production techniques. Further improvements in water-soluble and water-emulsifiable vehicles might very well necessitate radical adjustments in future manufacturing methods. In the fields of methylation and acrylation there is sufficient promise of substantial upgrading of film properties to warrant consideration of improved methods for their dispersion.

In addition to any developments that come from laboratories of the various pigment, solvent, and vehicle companies, there will still be considerable concentration on materials handling and pigment dispersion techniques. In both these fields there is ample opportunity for increased efficiency and greater reproducibility of results.

In the field of color matching there will undoubtedly be considerable expenditure of time in the search for instrumentation to minimize production delays during color matching.

Certainly the field of paint chemistry has broadened greatly since World War II. There is every indication that the paint industry will show greater advances than ever before in the next decade.

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(2E) Ambrose, C. M., Inc., Seattle, Wash., filling machine.

(3E) Berkeley Steel Construction Co., Inc., Berkeley, Calif., horizontal plate filter.

(4E) Continental Can Co., New York, N. Y., mail order can sealer.

(5E) Day, J. H., Co., Cincinnati, Ohio, pony-type mixer.

(6E) Devine, J. P., Mfg. Co., Inc., Pittsburgh, Pa., 200-gallon paste mixers.

(7E) Elgin Mfg. Co., Elgin, Ill., filling machine.

(8E) Gas Atmospheres, Inc., Cleveland, Ohio, 1000 cubic foot per hour inert-gas generating system.

(9E) Hapman Conveyors, Inc., Kalamazoo, Mich., induced-flow solids conveyor.

(10E) Heat & Control, Inc., San Francisco, Calif., radiant gas heating units.

(11E) Howe Scale Co., Rutland, Vt., platform scale.

(12E) Lehmann, J. M., Co., Lyndhurst, N. J., three-roll Sight-O-Matic mills.

(13E) Miller, Franklin P., & Sons, Inc., East Orange, N. J., ice crusher, Model 5.

(14E) Mixing Equipment Co., Rochester, N. Y., Lightnin' agitators for resin kettles, Models **414-TEC-102** and **414-TEC-403**; Models **VSE-3** and **VSE-7. 5** for premelt and thin-down tanks.

(15E) Morehouse Industries, Inc., Los Angeles, Calif., high speed stone mill.

(16E) Pangborn Corp., Hagerstown, Md., cloth screen dust collector.

(17E) Patterson Foundry and Machinery Co., East Liverpool, Ohio, 100-gallon pebble mill, 3 ft. 6 inches × 4 ft.; 250-gallon pebble mill, 4 × 5 ft.; 1000-gallon pebble mill, 8 × 6 ft.; 50-gallon steel ball mills, 2 ft. 6 inches × 3 ft. 6 inches; 250-gallon steel ball mills, 4 ft. 6 inches × 4 ft. 6 inches.

(18E) Remington Rand, Inc., New York, N. Y., Model 2 equipment: tabulator, summary punch, sorter, key punch, interpreter.

(19E) Toledo Scale Co., Inc., Toledo, Ohio, platform scales.

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chlorophyll by solvent extraction

American Chlorophyll Plant at Lake Worth, Fla.

MELVIN A. JUDAH, Assistant Editor

in collaboration with

EVERETTE M. BURDICK,[1] AND **ROBERT G. CARROLL**

American Chlorophyll Division, Strong, Cobb and Co., Inc., Lake Worth, Fla.

ONE of nature's most important organic compounds, chlorophyll, has become an object of intensive development in the past decade. Reaching a peak market in 1952, when products containing the green material attracted over $50,000,000 from American consumers (*4*), this young chemical specialty now appears to be getting its second wind. Stable consumer items, among them toothpastes, chewing gums, and candies, plus potential medical and pharmaceutical uses seem to offer a promising future.

Although earlier scientists had studied the green plant pigment, it was only in 1913 that the first significant research on its structure, separation, and properties was reported (*7*). This work, which won the 1915 Nobel prize for the German chemist Willstatter, serves as the basis for today's commercial production of chlorophyll. With modifications developed by the United States Department of Agriculture (*1*), those solvent extraction techniques are now the foundation of the chlorophyll industry in the United States. However, some chlorophyll and carotene have been produced commercially by chromatographic absorption from alfalfa leaf meal as described in a previous report (*2*).

Basically, the production methods developed by the Department of Agriculture involve extraction of carotene from dried leaf meal with petroleum ether and recovery of carotene by concentration of the extract. Chlorophyll and xanthophyll are then extracted from the meal with acetone. The acetone extract is dissolved in petroleum ether and the major portion of the acetone removed by washing with water. Xanthophyll is separated from this second extract by extraction with 85% methanol. Careful washing with water removes the alcohol from the petroleum ether solution, thus permitting the chlorophyll to be separated by precipitation. Chlorophyll is purified by reprecipitation from acetone–petroleum ether solution. Carotene and xanthophyll are purified by recrystallization.

As the most popular chlorophyll product, at present, is the water-soluble chlorophyllin form, American Chlorophyll and other producers use the basic USDA process modified with a saponification step (*6*). Thorough saponification of chlorophyll extract with a methanol–potassium hydroxide solution facilitates separation of the water-soluble chlorophyllin from the solvent, usually a hexane-acetone blend, for further purification and finishing. The water-soluble materials are, strictly speaking, not entirely soluble in water; all show the Tyndall phenomenon. A beam of light becomes visible when passed through these turbid solutions. Extract may be finished, instead, as oil-soluble chlorophyll by removal of plant waxes and oils. Solvent washings and evaporation complete the finishing of the oil-soluble products.

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[1] Present address, Chemical Consultant, 225 Harrison St., West Lafayette Ind.

Three major producers now employ solvent extraction processing with individual variations which are jealously guarded in the keenly competitive industry. From pilot scale production beginning in 1933, American Chlorophyll Division of Strong, Cobb and Co. at Lake Worth, Fla., has developed with the industry and now recovers not only chlorophyll and carotene, but xanthophyll, phytol, and research quantities of a number of derivatives. Keystone Chemurgic Corp. of Bethlehem, Pa., also extracts chlorophylls from alfalfa. The Glidden Co. extracts alfalfa at Buena Park, Calif., and ships the extract to Collett-Week at Ossining, N. Y., for finishing into chlorophyllins.

Organized in Washington, D. C., American Chlorophyll Co. conducted research activities and limited production in nearby Alexandria, Va., until 1947. All company operations were then shifted to the 17-acre site on the Palm Beach Canal in Lake Worth. More active processing research and design efforts brought this plant into large scale production in 1950, just in time to progress with chlorophyll's best market year to date, 1952. In that year the company merged with Strong, Cobb and Co., a pharmaceutical manufacturing firm of Cleveland, Ohio. When operating on a 24-hour-day extraction schedule, present facilities can produce 400 to 500 pounds of chlorophyll per day, depending on grade of alfalfa processed.

Products from the Lake Worth plant enter into a variety of applications. Chlorophyll extracted from the alfalfa leaf meal may be purified and marketed as an oil-soluble dye for lubricating oils, paints, and candles. A high purity oil-soluble product, which has had plant waxes removed by acetone extraction, goes into pharmaceuticals, foods, cosmetics, and ointments. However, over 90% of the chlorophyll extracted at Lake Worth becomes the water-soluble form, chlorophyllin. The most popular, sodium-potassium-copper chlorophyllin, finds use as a deodorizing agent in toothpastes, soaps, shampoos, candies, mouthwashes, deodorants, and pharmaceuticals. Chlorophyll, in various forms, was reportedly present in 1000 products that consumed 10,000 pounds of the green material per month in 1952. With many of the marginal products now off the market, a more stable 150 items are consuming about 2000 pounds per month in 1954.

Extract from the alfalfa leaf meal also contains the yellow carotenoid pigments, carotene and xanthophyll. Carotene, a fatty pigment of lipochrome, occurs in living vegetation in association with chlorophyll. In fact, an analysis of plant matter for carotene content may be used as an evaluation of its quality for chlorophyll extraction. In alfalfa, carotene occurs in the form of highly unsaturated isomers, α-carotene and β-carotene, having the formula $C_{40}H_{56}$. Both isomers are precursors of vitamin A. This has caused commercial interest in carotene as an additive to food products, particularly in margarine, since 1950 legislation removed federal restrictions on marketing of the yellow product. Carotenes are the natural coloring pigments in many yellow vegetables, butter, and eggs.

Xanthophylls, the hydroxy, keto, or hydroxy-keto derivatives of carotenes, may also be recovered in carotene purification. Research by the United States Department of Agriculture has stimulated interest in these derivatives as poultry feed supplements (*5*). Poultry fed a rich xanthophyll ration exhibits a healthy appearance of fatty tissue and skin to win good customer acceptance on butchers' shelves. Natural pigments have been isolated from fatty tissue, liver, eyes, blood serum, eggs, skin, and the feathers of fowls.

Saponification of chlorophyll or reaction with strong acids splits off the phytyl group from chlorophyll as the unsaturated alcohol phytol, $C_{20}H_{39}OH$. Laboratory quantities of phytol have been obtained by vacuum distillation of crude xanthophyll extract at Lake Worth. Phytol may be marketed as an intermediate for manufacture of vitamins E and K.

Lake Worth processing techniques were especially developed by American Chlorophyll, but they are not the only distinctive feature of the plant. Located almost 2000 miles from the source of most of its raw material, its economics of operation differ greatly from those reported in the first chlorophyll process article (*2*). Freight charges on alfalfa meal are an important factor in determining production costs; transportation costs from midwestern dehydrating plants amount to $20 to $30 per ton. However, long distance transportation of raw materials was not planned when the plant was built. In selecting the plant site, American Chlorophyll located near the ramie fields of the Everglades to use the salvaged leaves of this fiber-bearing plant. Chemical defoliation methods eliminated this potential source of chlorophyll prior to start-up of operations.

Other factors have allowed profitable operation of the Florida plant using, instead of ramie, alfalfa leaf meal shipped from distant dehydrating plants. An ideal climate permitted low cost plant construction; most processing units are in the open on concrete slabs. Construction costs for sheltering buildings was minimized; hazards of fire and explosion were reduced. Unusually good living and working conditions maintain high morale; labor is plentiful. Income from a ready market for extracted alfalfa meal at local dairies virtually offsets the freight charges on raw material. If agricultural researchers are successful in developing ramie harvesting equipment which will also recover the leaves for chlorophyll processing, the plant may yet utilize that economical raw material.

One project conducted at the University of Florida had as its objectives more complete data on the solvent extraction of chlorophyll from ramie leaves. Early chemists reported that chlorophyll derived from a wide variety of plant matter possesses uniform properties after separation and purification regardless of source (*7*). Research efforts of modern producers toward development of new sources confirm these results. If current projects meet with success, the final major hurdle may be one of convincing producers of consumer items that the chlorophyll they are buying is the same as that from alfalfa.

Hexane-Acetone Blend Extracts Chlorophyll and Carotene from Dehydrated Alfalfa Meal

Considerable research has been conducted on recovery of chlorophyll from various plant sources; however, all present commercial production is from alfalfa. It is the most readily available source of chlorophyll and, perhaps more important, many purchasers of chlorophyll derivatives for consumer products specify the material. Such specifications must be strictly honored; slight change in color or taste is reflected in consumer acceptance.

American Chlorophyll alfalfa buyers obtain samples of dehydrated leaf meal from southwestern or midwestern dehydrators. Samples are sent to Lake Worth for assay to determine chlorophyll, carotene, xanthophyll, protein, moisture, and fiber content prior to shipment. Although buyers may not always be able to purchase such a high grade meal, one with the following analysis is considered ideal for processing:

Carotene (min.), I.U./lb.	200,000
Protein, %	20
Fiber (max.), %	20
Fat (approx.), %	5
Moisture, %	7

Meal containing 200,000 units of vitamin A per pound yields 9 to 10 pounds of processed chlorophyll per ton, while that containing 150,000 units yields only 7 to 8. For this reason, accurate assays are always completed on each lot of meal prior to purchase. Freight charges on a carload often amount to as much as $750.

In addition to the economic importance of meal assays, advance meal analyses provide means of estimating the amounts of reactants, such as hydrochloric acid, potassium hydroxide, and copper sulfate that will be needed for scheduled processing. Variations in moisture, fat, wax, and steroid content of a particular lot of alfalfa influence processing and refining steps necessary to obtain uniform products. Meal low in carotene has

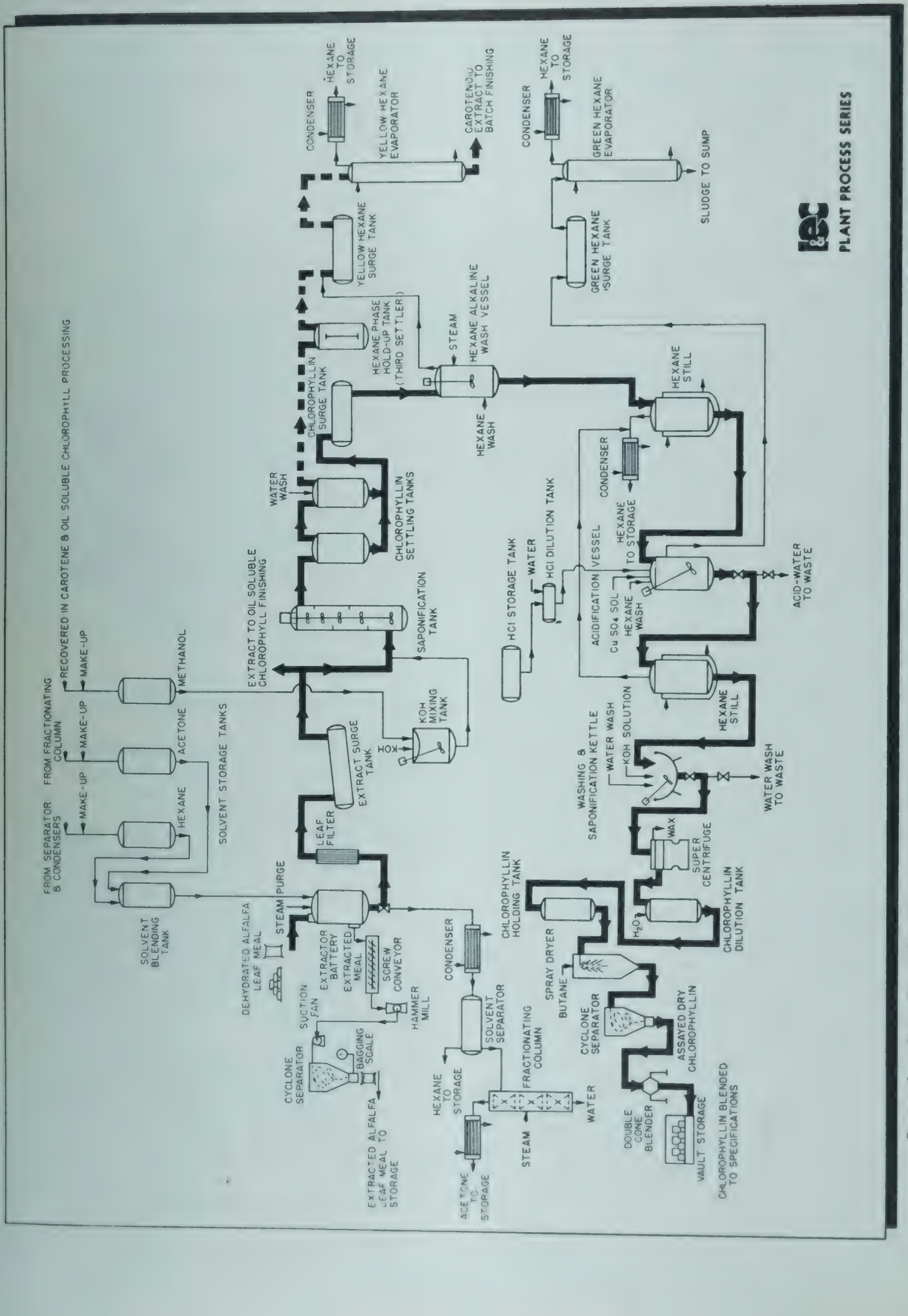
FROM SEPARATOR & CONDENSERS
MAKE-UP
FROM FRACTIONATING COLUMN
MAKE-UP
RECOVERED IN CAROTENE & OIL SOLUBLE CHLOROPHYLL PROCESSING
MAKE-UP
SOLVENT BLENDING TANK
HEXANE
ACETONE
METHANOL
SOLVENT STORAGE TANKS
DEHYDRATED ALFALFA LEAF MEAL
STEAM
STEAM PURGE
EXTRACTOR BATTERY
EXTRACTED MEAL
SCREW CONVEYOR
SUCTION FAN
HAMMER MILL
CYCLONE SEPARATOR
BAGGING SCALE
EXTRACTED ALFALFA LEAF MEAL TO STORAGE
LEAF FILTER
EXTRACT SURGE TANK
KOH
KOH MIXING TANK
EXTRACT TO OIL SOLUBLE CHLOROPHYLL FINISHING
SAPONIFICATION TANK
CHLOROPHYLLIN SETTLING TANKS
WATER WASH
CHLOROPHYLLIN SURGE TANK
HEXANE PHASE HOLD-UP TANK (THIRD SETTLER)
STEAM
HEXANE ALKALINE WASH VESSEL
HEXANE WASH
YELLOW HEXANE SURGE TANK
YELLOW HEXANE EVAPORATOR
CONDENSER
HEXANE TO STORAGE
CAROTENOID EXTRACT TO BATCH FINISHING
CONDENSER
SOLVENT SEPARATOR
HEXANE TO STORAGE
FRACTIONATING COLUMN
STEAM
WATER
ACETONE TO STORAGE
HCl STORAGE TANK
WATER
HCl DILUTION TANK
ACIDIFICATION VESSEL
Cu SO4 SOL
HEXANE WASH
HEXANE TO STORAGE
CONDENSER
HEXANE STILL
HEXANE STILL
ACID-WATER TO WASTE
GREEN HEXANE SURGE TANK
GREEN HEXANE EVAPORATOR
CONDENSER
HEXANE TO STORAGE
SLUDGE TO SUMP
WASHING & SAPONIFICATION KETTLE
WATER WASH
KOH SOLUTION
WATER WASH TO WASTE
WAX
SUPER CENTRIFUGE
CHLOROPHYLLIN DILUTION TANK
H_2O
CHLOROPHYLLIN HOLDING TANK
SPRAY DRYER
BUTANE
CYCLONE SEPARATOR
ASSAYED DRY CHLOROPHYLLIN
DOUBLE CONE BLENDER
VAULT STORAGE
CHLOROPHYLLIN BLENDED TO SPECIFICATIONS
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Figure 1. Flow Sheet for Production of Chlorophyllins, American Chlorophyll Division, Strong, Cobb and Co., Lake Worth, Fla.

a correspondingly low chlorophyll content and requires more processing chemicals to remove undesirable plant materials.

Shipment and storage of alfalfa must be carefully controlled as damp meal will mold, rendering it unfit either for extraction of chlorophyll or use as a livestock feed after processing. Susceptibility of carotene to oxidation by peroxidase and other enzymes limits the time meal may be stored prior to processing. Studies conducted by the United States Department of Agriculture indicate that up to 70% of the carotene present in dehydrated alfalfa meal may be lost during 5 months of storage in a nonrefrigerated warehouse (*3*).

To prevent this carotene loss, American Chlorophyll normally does not stock meal longer than one month prior to extraction, and when possible maintains an even closer buying schedule. Extracted meal may be stored indefinitely if moisture content is 7.0% or less. However when atmospheric conditions increase moisture content about 10 to 12% extracted meal cannot be stored safely longer than 3 or 4 weeks.

An enclosed warehouse containing 4000 square feet of floor space provides storage for about 180 tons of alfalfa meal, either raw or extracted in varying proportions. Burlap bags containing 100 pounds of raw meal are unloaded from freight cars or trucks onto conveyors which carry them into the warehouse where they are removed and stacked by hand.

The extractor battery consists of eight vertical cylindrical mild steel vessels of 1500-gallon capacity and two of 2000-gallon capacity. The two large vessels were installed during accelerated plant expansion. Differences in size of extractors does not affect processing. Solvent circulation lines permit operation of the battery as a series flow batch diffusion unit of four extractors or operation of any number of extractors in parallel flow. Normally, a 24-hour schedule utilizes four vessels operating as a unit in series flow. The six other off-stream extractors are in various stages of cleanout and recharging. Each extractor requires about 2 hours for charging, is on stream for a 3-hour period, and goes off stream 5 hours for steam scavenging of solvent followed by cleanout. As a newly charged extractor comes on stream the fourth extractor in the unit goes off. Lean solvent blend enters the extractor that has been on stream longest, then passes through the next to the last one charged, and finally through the latest extractor placed on stream. A solvent blend of 80 to 90% hexane with acetone thus contacts the meal in three extractors by series flow. Centrifugal pumps circulate the solvent blend at 30 to 35 gallons per minute. Extract rich in chlorophyll and carotene goes from the last extractor charged through one of two leaf filters (*2E*) to the extract surge tank. To ensure a uniform chlorophyll concentration in the extract, a freshly charged extractor is filled with extract from the surge tank prior to placing it on stream. In normal series batch diffusion operations, 1500 gallons of extract and about 6000 gallons of hexane-acetone blend solvent contact the two-ton meal charge in each extractor.

At Lake Worth about 90% of the recoverable chlorophyll and carotenoids are stripped from the meal during the first hour of extraction. Extractors remain on stream the additional 2 hours to strip the last 10% of these products because of the large amount of labor and time required for off-stream operations.

Circulation pumps withdraw over two thirds of the extract from the meal in a vessel going off-stream. Scavenging steam, admitted at the top of the extractor, forces remaining solvent from the meal cake to the solvent blend tank. Last traces of solvent and steam are condensed, and the solvent is recovered by gravity separation.

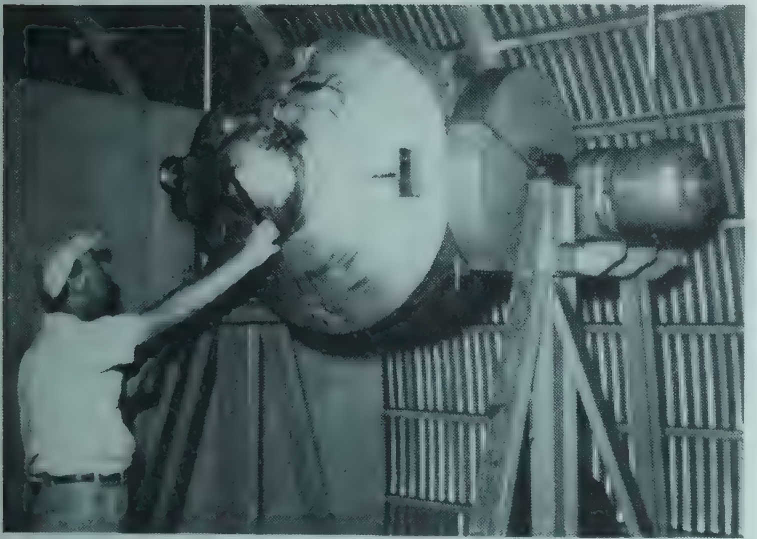
When market conditions warrant, the Lake Worth plant may go on a curtailed operating schedule, producing 50 to 75 pounds of chlorophyll in an 8- or 10-hour day. At such times the extraction battery on stream consists of three 1500-gallon vessels each containing a 2-ton charge of alfalfa meal. After each vessel is charged it is almost filled with 1300 gallons of hexane-acetone solvent blend. Centrifugal pumps recirculate solvent through each extractor for one hour. A rich extract is drawn off, and blend solvent is circulated through the three extractors in parallel flow for an additional 2 hours. When scheduling permits, the first extract containing about 0.65% chlorophyll by weight, as

Potassium hydroxide is thoroughly blended with methanol in 2 mix tanks to maintain carefully controlled solution for saponification of chlorophyll extract

Outdoor construction of extractor battery permits low cost construction and minimizes fire and explosion hazards from solvent leaks

Magnesium chlorophyllin is converted to more stable copper form by acidification and reaction with copper sulfate in mild steel tank battery

Open stainless steel kettles are used for first chlorophyllin finishing steps, saponification, and water washing, ensuring removal of water-soluble impurities



Mixing batches of dry chlorophyllin in this double-cone blender yields a product that meets strict consumer specifications

From these nozzles at top of spray dryer tower a chlorophyllin fog quickly becomes potassium copper chlorophyllin powder—Lake Worth's main product

compared with a 0.4% extract from a series flow batch diffusion, will be finished as oil-soluble chlorophyll. Oil-soluble materials finished from the rich extract provide a uniformly high purity product. Lean extracts may be finished more economically through the several processing and finishing steps required for chlorophyllins.

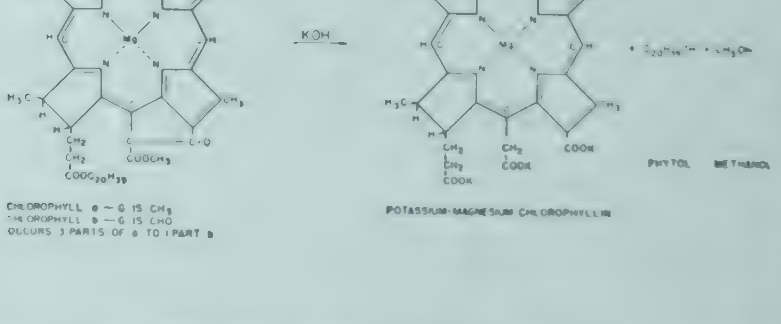
A cycloidal gear pump forces extract from all extraction units through one of two leaf filters (*2E*) to remove meal fines before extract enters the surge tank. To further ensure that no meal passes into chlorophyll or chlorophyllin finishing steps, the 4000-gallon cylindrical surge tank is elevated about 10 inches at the discharge end. Operators make frequent inspections of sight glasses to detect possible presence of any meal fines.

Cleanout of meal from extractors consumes valuable time and labor, especially during continuous operations. Meal sets up into a hard, fibrous cake in the extractors, requiring a crew of four men 2 hours to empty the vessel. When market demands justify continuous production, time delays are directly costly. Labor costs themselves also become an important factor

After digging cake out of vessels, large chunks of meal are broken with axes and transferred to a hammer mill (*8E*) by a screw conveyor. A pneumatic conveyor system (*8E*) carries the ground meal from the hammer mill to the warehouse where it is recovered in a cyclone collector. Meal may be bagged in 85-pound bags directly or may first be mixed with molasses and pelletized (*8E*). Bags of extracted meal are stitched, tagged with proper analysis, and stacked to await sale as livestock feed.

Saponification, Coppering, and Finishing Produce Water-Soluble Chlorophyllins

The hexane-acetone solvent blend extracts contain not only chlorophyll, carotene, and xanthophyll but also the undesired plant materials—waxes, oils, steroids, and lipoids. The first purification step in the processing of chlorophyllins (Figure 1) consists of saponifying the chlorophyll by contacting the extract with a methanolic–potassium hydroxide solution. This solution is about one half saturated or 15 to 25% potassium hydroxide by weight. Methanolic–potassium hydroxide accomplishes virtually complete saponification of chlorophyll and retards formation of an emulsion with plant matter. Chlorophyll is thereby converted to a water-soluble form called sodium–potassium magnesium chlorophyllin in trade terminology. Actually the chlorophyllin produced is predominantly the tripotassium salt, however a very small percentage of sodium ion picked up in the processing operation originally gave rise to the nomenclature now used by the trade. The following reaction occurs:



A phytyl group and a methyl group are replaced with potassium, and the carbocyclic ring is opened, yielding phytol and methanol. The water-soluble chlorophyllin may then be separated from carotenoids and other unsaponified plant matter by water washing and gravity settling.

Potassium hydroxide and methanol are mixed in two 750-gallon vertical mixing tanks and injected into the extract feed line just ahead of the saponification tank. Extract and methanolic–potassium hydroxide come into intimate contact in the vertical saponification mixer. The mixture enters tangentially near the bottom of a 250-gallon vertical mixer. Five propellers, driven from a central shaft by a 3-hp. explosionproof motor mounted atop the tank, move the liquor upward through the mixer around four side-wall baffles. Effluent from the saponification mixer consists of an intimately mixed two phase system. Hexane contains the bulk of the carotenoids, waxes, and unsaponified plant matter; chlorophyllins are carried by the acetone-methanol-water phase.

Flow rate of the mixture passing through the saponification tank is governed by colorimetric assay of chlorophyll in the extract. Samples are taken every half hour; results are made available to the operator within 5 minutes.

Mixed effluent from the saponification step is pumped to the first of three settlers. Each of these vertical cylindrical tanks has a capacity of 1600 gallons. About 90% of the potassium magnesium chlorophyllin solution settles as the bottom layer in the first settler. At 4-hour intervals, this solution is drawn off and pumped to the 2500-gallon chlorophyllin surge tank. The top hexane layer passes on to the second settler for water washing to separate the remaining 10% of chlorophyllin. Operators draw off the bottom chlorophyllin layer from the second settler daily. The yellow hexane top layer containing carotenoids passes through the third settler, which serves only as a check on the efficiency of the saponification step. In normal operations the sight glass on the third settler will contain yellow hexane. However, if saponification of chlorophyll has not been complete, the glass may contain a green solution. Should green solution appear, the saponification process is shut down, and troubles are determined and corrected prior to further processing.

A centrifugal pump moves carotenoid extract from the third settler to the 4000-gallon yellow hexane surge tank. A vertical long tube natural circulation evaporator (*1E*), fed from this surge tank, recovers hexane and concentrates carotenoid extract for carotene and xanthophyll finishing steps.

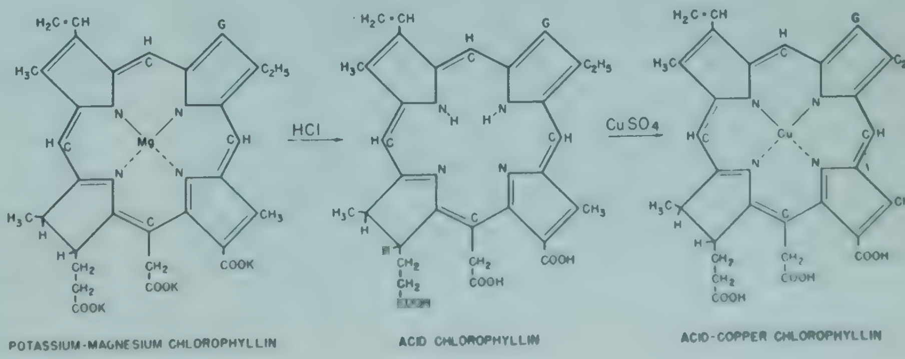
To ensure removal of all carotenoids from the chlorophyllin phase, the solution from the chlorophyllin surge tank is washed batchwise with a 90 to 95% hexane-acetone blend in a 3300-gallon mild steel tank. Volume of the batch washed depends on the concentration of chlorophyllin; a typical charge containing 3% chlorophyllin by weight would be about 4150 pounds or 500 gallons of solution. Following 30 minutes of washing with agitation, steam is introduced directly into the vessel raising the temperature of the washed mixture to about 104° F., the optimum temperature for separating the carotenoid phase from the chlorophyllin. Hexane containing carotenoids is then drawn off the top and sent to yellow hexane surge.

Chlorophyllin solution goes to a steam-jacketed still for complete removal of solvent. Hexane is recovered, some as an azeotrope with acetone or methanol, and returned to solvent storage tanks. Distillation must be controlled carefully as the chlorophyllin solution foams highly when hexane has been removed. At first appearance of foam the operator cuts off steam, and the chlorophyllin solution is pumped to an acidification vessel.

Naturally occurring magnesium chlorophylls or potassium magnesium chlorophyllins do not possess the high tinctorial strength and light stability desired in commercial derivatives. Substitution of other metals for the magnesium atom in the chlorophyllin molecule takes place in the acidification and coppering vessels by the two step reaction. ⟶

By carefully controlled acidification, two hydrogen atoms replace the magnesium; reaction with copper sulfate solution introduces the copper atom into the center of the chlorophyllin molecule.

The solution in the acidification vessel is assayed for chlorophyllin content and then diluted with water. Agitation during addition of copper sulfate solution mixes the charge thoroughly. Prior to addition of acid, the mixture has a pH of about 10. Acidification is carried out using 37.5% hydrochloric acid diluted with about an equal volume of water.



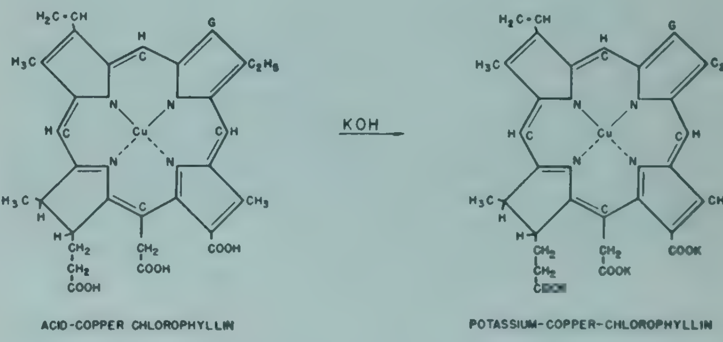
Addition of acid reduces the pH of the solution stepwise to 1.5. After agitation, the acidified mixture stands until the acid-copper chlorophyllin rises to the top of the vessel as a thick cake. This cake carries varying quantities of coagulated waxes, sterols, and other undesired matter. Low solubility of the copper-acid chlorophyllin in either a hexane-acetone solvent or in water permits removal of oil- and water-soluble impurities by washing.

Acid water discharged from the bottom of the acidification vessels goes to a waste sump, from which it is fed into the plant's 80,000-gallon-per-hour condenser water discharge, thus preventing pollution of the Palm Beach Canal adjacent to the plant site.

A wash of 90 to 95% hexane-acetone removes the waxes, sterols, and other oil-soluble impurities from the cake. Agitation continues for 30 minutes after addition of solvent. Following removal of oil-soluble matter, the copper-acid chlorophyllin precipitates during a 4-hour settling period. Solvent is then drawn off the top and pumped to the green hexane surge tank for hexane recovery by a vertical long tube natural circulation evaporator (*1E*). Solvent washings may be repeated to ensure purity. Chlorophyllins produced from a good grade of alfalfa normally need only one washing; however, those from poorer grades (150,000 units of vitamin A or less per pound) may require two or three washings to remove all undesired plant matter. When the precipitate reaches a purity exceeding 80%, it is pumped to a 1000-gallon jacketed still for evaporation of traces of solvent prior to finishing.

Chlorophyllin slurry from the still goes to a 250-gallon stainless steel steam jacketed kettle in the finishing room. Water washing removes traces of water-soluble impurities from the insoluble copper-acid chlorophyllin. After a few minutes of mixing, agitation is stopped and the chlorophyllin floc floats to the top; water is drawn off and washing is repeated three or four times. During washings the slurry becomes nearly neutral.

To reconvert the chlorophyllin into its water-soluble form, the slurry is saponified with a solution of potassium hydroxide. Concentration of chlorophyllin in solution determines the amount of potassium hydroxide required to complete saponification. During the following saponification, pH of the chlorophyllin solution increases to about 11.5:



Filtration of the saponified chlorophyllin solution through a centrifuge (*6E*) removes trace quantities of plant waxes. The operator adjusts concentration of the filtrate to 10 to 15% solids by dilution with water. Potassium-copper chlorophyllin solution is then pumped to a 250-gallon stainless steel holding tank in the spray dryer building. Clarified aqueous solutions of

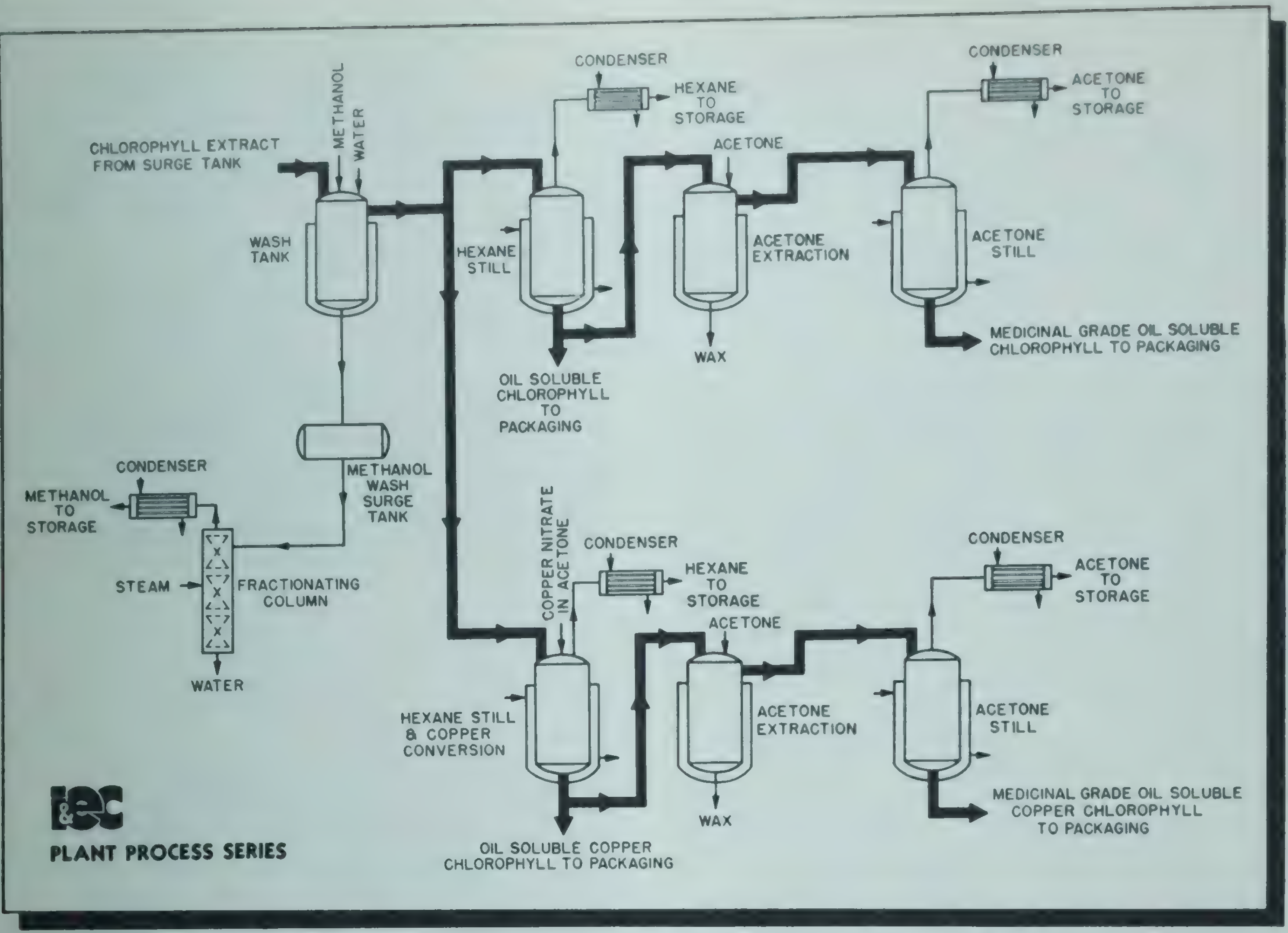

CHLOROPHYLL EXTRACT FROM SURGE TANK
METHANOL
WATER
WASH TANK
CONDENSER
HEXANE TO STORAGE
HEXANE STILL
OIL SOLUBLE CHLOROPHYLL TO PACKAGING
ACETONE
ACETONE EXTRACTION
WAX
CONDENSER
ACETONE TO STORAGE
ACETONE STILL
MEDICINAL GRADE OIL SOLUBLE CHLOROPHYLL TO PACKAGING
METHANOL WASH SURGE TANK
CONDENSER
METHANOL TO STORAGE
STEAM
FRACTIONATING COLUMN
WATER
COPPER NITRATE IN ACETONE
CONDENSER
HEXANE TO STORAGE
HEXANE STILL & COPPER CONVERSION
OIL SOLUBLE COPPER CHLOROPHYLL TO PACKAGING
ACETONE
ACETONE EXTRACTION
WAX
CONDENSER
ACETONE TO STORAGE
ACETONE STILL
MEDICINAL GRADE OIL SOLUBLE COPPER CHLOROPHYLL TO PACKAGING
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Figure 2. Flow Sheet for Processing of Oil-Soluble Chlorophylls

chlorophyllins find some market demand, but the bulk of Lake Worth production is finished as the spray dried product.

Sodium-Potassium-Copper Chlorophyllin Is Spray Dried, Blended to Customer's Specifications

A six-nozzle sprayer atomizes sodium-potassium-copper chlorophyllin near the top of a 40-foot stainless steel drying tower (*3E*). Butane-fired burners located above a perforated plate at the top of the tower heat air to 650° F. giving the tower a drying capacity of 450 pounds of water per hour. The heated air blown down through the tower makes intimate contact with chlorophyllin fog, producing hollow beads of dried chlorophyllin which are then recovered in a double cyclone collector.

Batches of chlorophyllin may vary in physical properties and concentration, but customer's specifications for the product currently selling at $45 per pound are rigid. Variations in grade of alfalfa meal sometimes influence product purity. Extract from low grade meal carries relatively large quantities of waxes, lipoids, and other plant matter, traces of which may appear in product assay. Controlled blending to individual specifications has become an essential art at Lake Worth. From assays of various batches stored in a 1200-cubic foot reinforced concrete vault, the blender operator determines quantities of selected batches required to obtain a specified blend. Using a 13-cubic foot double-cone blender (*5E*), the operator blends in batches of 300 pounds, unless special orders limit blends to a smaller quantity. On completion of blending, the dry chlorophyllin is assayed and packed in polyethylene-lined 50-pound fiber drums. Drums are sealed, labeled with certified assay, and stored in the vault. When market demands require excess stocks, the final "process" step consists of transfer of surplus chlorophyllin to the First National Bank vault at Palm Beach.

Purity of the spray dried chlorophyllins normally exceeds 90%, and spectrophotometric assays have in some cases been over 100% of theoretical. Spray dried sodium-potassium-copper chlorophyllin is readily soluble in cold water, the blue-black powder granules giving a deep green solution. When dissolved in distilled water the solution has a pH of about 10; however, the chlorophyllin becomes insoluble at a pH lower than 6.5. Purification and finishing at Lake Worth concentrate the chlorophyll more than 200-fold—from 0.4% in the alfalfa meal extract to a purity exceeding 90%.

In addition to chlorophyllin solutions and the dried sodium-potassium-copper chlorophyllin, the American Chlorophyll plant prepares a variety of water-soluble products to special customer specifications. Light saponification of chlorophyll extract produces an alkaline magnesium chlorophyllin. Purification consists of washing with acetone, hexane, and isopropyl alcohol; after which the material is dried on a stainless steel steam tray. The product containing about 25% chlorophyllin may be sold in the dry form or diluted to a 4% solution for such use in mouth wash formulations. Another special product may be produced by mixing refined sodium-potassium-copper chlorophyllin with reconstituted animal protein. After drying, this material, containing 5% chlorophyllin by weight, is sold as an additive for dog food.

Chlorophyllins may also be prepared with metals other than copper being substituted for magnesium. Alkaline chlorophyllins of iron, cobalt, or nickel are also available. Other metallic chlorophyllins may be prepared for pharmaceutical research.

Batch Finishing Produces Variety of Oil-Soluble Chlorophylls

Prior to the introduction of the water-soluble chlorophyllins as deodorizing agents, the bulk of the chlorophyll produced by American Chlorophyll was in the oil-soluble form. This green viscous liquid finds application as a coloring pigment in foods, soaps, cosmetics, pharmaceuticals, lubricating oils, and paints. At a concentration of 4% chlorophyll by weight, it is a free flowing, green-yellow liquid; highly refined to 10 and 15% grades it becomes a viscous dark green liquid. All natural chlorophyll grades fluoresce a blood red. Although oil solubles do not have the market demand of the chlorophyllins, the Lake Worth plant prepares several grades by batch finishing (Figure 2).

When extraction battery scheduling permits, the oil-soluble chlorophyll finishing operator uses the rich extract which has been recirculated during the first hour of parallel flow extraction. A comparatively lean extract from series flow operations may be used; it requires more washings to obtain a high purity product.

The first finishing steps for the oil-soluble product consists of methanol and water washings of a 1500-gallon extract charge in a steam-jacketed still. Ten washings, each with 25 gallons of methanol, remove plant waxes and xanthophyll. Methanol washings are withdrawn to a surge tank for recovery of methanol by fractionation. Several washings with about 10 gallons of water remove the last traces of methanol from the extract and are also fractionated to recover methanol. Evaporation of hexane-acetone solvent yields the 4% grade of oil-soluble chlorophyll. If several grades of chlorophyll are being finished at one time, the extract may be transferred to another still for evaporation of the hexane. To produce a higher grade product, the liquid 4% chlorophyll then goes to another still where acetone washing extracts chlorophyll leaving small quantities of plant waxes as a precipitate. Acetone-chlorophyll extract is drawn off the top to another still where evaporation of the acetone yields a concentrated oil-soluble product containing 17% chlorophyll by weight. Blending with cottonseed oil adjusts chlorophyll concentration to either 10 or 15% for use in pharmaceuticals.

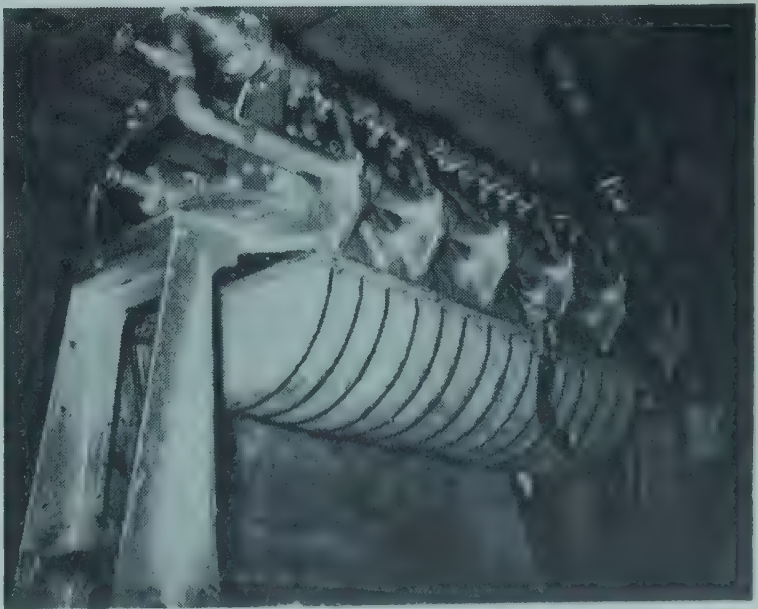
Oil-soluble chlorophylls may also be coppered to provide a product with higher tinctorial strength and improved light fastness. To substitute copper for magnesium in the chlorophyll molecule, a methanol and water washed extract is transferred to another still and treated with a saturated solution of copper nitrate in acetone. The reaction proceeds with agitation for one hour, after which copper-substituted chlorophyll is recovered by evaporation of solvent. This viscous, blue-green liquid contains about 13% copper chlorophyll by weight; blending with cottonseed oil adjusts concentration to customer specifications. Extraction of copper chlorophyll with acetone removes plant waxes; evaporation yields a product containing 18% copper chlorophyll, which may be blended to specified concentrations for pharmaceutical applications. Oil-soluble chlorophylls may also be stabilized with metals other than copper for special orders.

Carotene, Xanthophyll, and Phytol Are Finished in Limited Quantities

Chlorophyllins and chlorophyll comprise the bulk of Lake Worth production, but carotene, xanthophyll, and phytol are also recovered by batch purification of the hexane phase of meal extract (Figure 3). Carotenoid extract from the yellow hexane evaporator may contain traces of chlorophyll. Presence of even trace quantities of the high tinctorial strength green material may discolor refined carotene, unless completely removed. A very "hard" saponification using a supersaturated solution of potassium hydroxide mixed with methanol converts chlorophyll to the water-soluble chlorophyllin form. A 200-gallon charge of carotenoid extract is placed in a 500-gallon mild steel still Addition of potassium hydroxide solution and methanol creates a highly exothermic reaction; a reflux condenser atop the still prevents boilover or loss of hexane vapors. When the reaction is complete, the carotenoid extract goes to a 1500-gallon jacketed still for extraction of carotenoids with hexane. During washing an emulsion may form; if so, it is broken by introducing steam into the jacket and adding a small quantity of acetone to the

Two long tube natural circulation evaporators recover hexane from extraction and washing steps

Washing acid chlorophyllin precipitate with hexane removes plant waxes and sterols; last traces of hexane are removed in steam-jacketed still ahead of finishing operations



Pressure leaf filter removes wax impurities from carotene extract after saponification and washing eliminate traces of chlorophyll hexane extract. This extract is drawn off the top layer of the vessel and tranferred to a similar still where three washings with water ensure removal of traces of the water-soluble chlorophyllin. Washings containing water, acetone, and small quantities of methanol go to the solvent separator for gravity separation and to the fractionating column for recovery of acetone.

Steam distillation evaporates hexane. The carotenoid extract, containing carotene, xanthophyll, and phytol produced during saponification of chlorophyll, goes to a stainless steel steam jacketed kettle for evaporation of residual hexane to the atmosphere. This concentrated carotenoid extract, which still contains plant waxes, is transferred to an 800-gallon tank, and slurried with 600 gallons of acetone. Carotene, xanthophyll, and phytol are extracted. Filtration of the slurry through a pressure leaf filter (*4E*) followed by another through a plate-and-frame filter (*7E*) remove plant wax residues. Evaporation of acetone in a steam-jacketed still recovers the dewaxed carotenoids with phytol. Wax is removed from the filters and placed in a steam-jacketed still for recovery of acetone; wax residues are recovered and stored in drums for future market possibilities.

The dewaxed carotene, xanthophyll, and phytol concentrate has residual acetone evaporated in a jacketed stainless steel kettle. A wash, consisting of 90 to 95% methanol with water, extracts xanthophyll and phytol. This extract goes to a steam-jacketed still for methanol recovery. The residual crude xanthophyll-phytol paste is then packaged for marketing as a poultry feed supplement. Phytol may be recovered from this concentrate by vacuum distillation in glass equipment for use in the preparation of vitamins E and K.

Carotene paste from the methanol-xanthophyll extraction is transferred to another stainless steel kettle where methanol is evaporated to the atmosphere. An isopropyl alcohol wash crystallizes carotene from the residue. Crystals are filtered in a 32-cm. Büchner funnel, slurried with pentane, decanted, and dried under radiant heat. Slurrying hot filtrate with additional isopropyl alcohol recovers more carotene crystals. Recovered carotene, 85% pure, consists of both the beta and the alpha forms in a ratio of about 2:1. Carotene crystals are packed in 50-gram tins and sealed under an atmosphere of nitrogen.

Variations in Raw Material and Scheduling, Require Both Art and Science in Process Control

Control of the several processing steps at Lake Worth has developed into an art from early pilot scale research tempered with experience under a variety of conditions. Little instrumentation may be found; most of the control techniques are based on evaluations of periodic laboratory assays by experienced production supervisors. Rotameters installed in flow lines ahead of each chlorophyllin settling tank comprise the plant's only flow measuring devices. pH meters and recorders serve to control rate of acidification in the coppering step. Virtually no instrumentation has been used in the batch operations for finishing oil-soluble chlorophylls and carotenoids. Automatic controls are not used, primarily because most of the operations in the plant are batchwise. Wide variations in densities and other physical properties of materials processed to product finishing steps are also factors that render automatic control unfeasible. Flow rates in many of the washing steps vary, too, because of differences in raw material processed.

Incoming raw materials are analyzed prior to purchase and again before extraction. Chlorophyll assays are by Goldfisch fat extraction apparatus, a modified Soxhlet type extractor, followed by colorimetric analysis of the extract. Carotene and xanthophyll are determined by chromatographic separation from a solvent extract followed by spectrophotometric analysis of the products. Protein analysis is by Kjeldahl digestion; moisture content by oven drying; and fiber by method of the Association of Official Agricultural Chemists. Rapid laboratory colorimetric analyses control flow rates and concentrations of reagents during

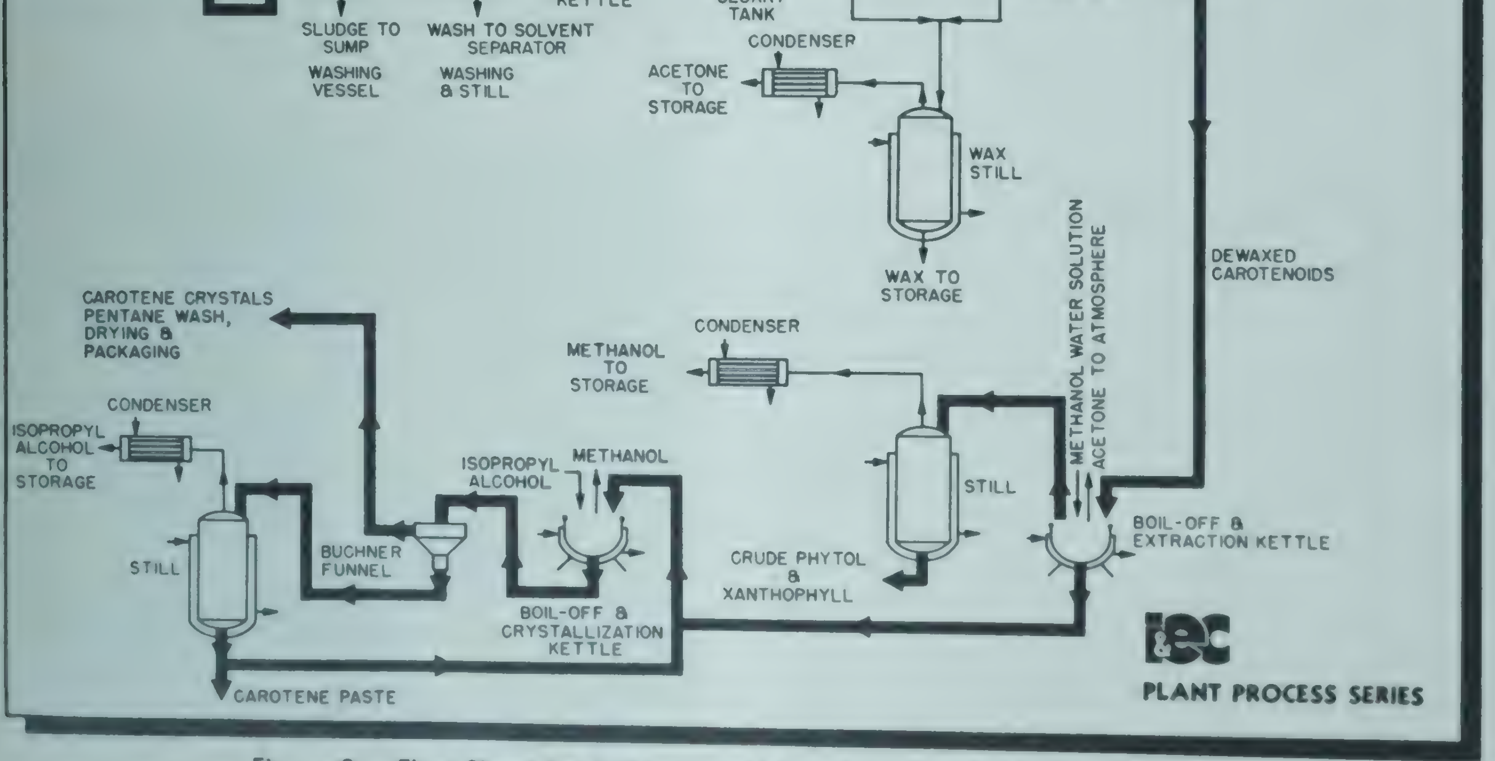

HEXANE TO STORAGE
CONDENSER
CAROTENOID EXTRACT FROM YELLOW HEXANE EVAPORATOR
METHANOL
KOH SOLUTION
HEXANE WASH
ACETONE WASH
WATER
HEXANE TO ATMOSPHERE
ACETONE
SAPONIFICATION TANK WITH REFLUX CONDENSER
PRESSURE LEAF FILTER
BOIL-OFF KETTLE
SLURRY TANK
PLATE & FRAME FILTER
SLUDGE TO SUMP
WASH TO SOLVENT SEPARATOR
WASHING VESSEL
WASHING & STILL
CONDENSER
ACETONE TO STORAGE
STILL
CONDENSER
ACETONE TO STORAGE
WAX STILL
WAX TO STORAGE
DEWAXED CAROTENOIDS
METHANOL WATER SOLUTION
ACETONE TO ATMOSPHERE
CAROTENE CRYSTALS PENTANE WASH, DRYING & PACKAGING
CONDENSER
METHANOL TO STORAGE
CONDENSER
ISOPROPYL ALCOHOL TO STORAGE
ISOPROPYL ALCOHOL
METHANOL
STILL
BOIL-OFF & EXTRACTION KETTLE
STILL
BUCHNER FUNNEL
CRUDE PHYTOL & XANTHOPHYLL
BOIL-OFF & CRYSTALLIZATION KETTLE
CAROTENE PASTE
I&EC
PLANT PROCESS SERIES

Figure 3. Flow Sheet for Purification of Carotene, Xanthophyll, and Phytol

processing, except in final purification steps where more precise analyses with the Beckman quartz spectrophotometer provide data for control.

Spray dried sodium-potassium-copper chlorophyllin is assayed for concentration and absorbency ratio by spectrophotometric methods specified by the Council on Pharmacy and Chemistry of the American Medical Association in their publication, "New and Non-Official Remedies." Nitrogen content of the chlorophyllin is determined by Kjeldahl digestion; copper and the amount of ionic copper freed at a pH of 3 are analyzed by flame techniques using a quartz spectrophotometer. Analyses also determine moisture, potassium, and sodium content as well as the pH and solubility of the dried chlorophyllin. Concentration data controls blending to specific wishes of individual customers.

A simple volumetric analysis of solvent from the blend tank determines the percentage of hexane. By shaking a known volume of solvent with a measured quantity of water in a graduated cylinder, and observing the change in volume of the hexane phase, the composition of the blend is determined Frequent determinations ensure an optimum solvent blend for extracting plant matter from alfalfa meal.

Extraction of chlorophyll and carotene requires from 350 to 450 gallons of hexane and 60 to 90 gallons of acetone per pound of finished material. Additional quantities are used for washing products during purification steps. Recovery of solvent must be maintained at a maximum to produce economically chlorophyllins, chlorophylls, and the carotenoids. Two vertical long tube natural circulation evaporators (*1E*), and two steam-jacketed stills recover hexane from chlorophyllin processing. Distillation of hexane washings in carotene and oil-soluble chlorophyll finishing recovers additional amounts of hexane. Some of the hexane is recovered as an azeotrope with acetone but may be used again in processing. A solvent separator also recovers hexane by gravity separation of the solvent scavenged from off-stream extractors. The water-soluble bottom layer from this 2000-gallon horizontal cylindrical steel tank goes to a fractionating tower packed with one-inch Raschig rings for recovery of acetone. Distillation of washings and wax residues in carotene and oil-soluble chlorophyll finishing recovers additional quantities of acetone. Methanol is recovered by fractionating washings from oil-soluble chlorophyll processing and by distillation of xanthophyll and phytol extract. Distillation of the filtrate from carotene crystals recovers isopropyl alcohol.

Utility services are simplified at the Lake Worth plant. Two fully automatic marine boilers burn about 8000 gallons of bunker C fuel oil per month to generate 16,000 pounds of steam per hour for process heating and drying. Boiler make-up is 100% as no heating steam is recovered. Chlorophyllin drying operations consume 120 gallons of butane per week when the plant operates on a 8-hour-per-day schedule. A local public utility supplies 65,000 kilowatt hours per month, which provides electric power for materials transfer, lighting, mixing, and blending operations. Solvent recovery utilizes about 80,000 gallons of condenser water per hour from three wells.

Some corrosion problems arise in the acidification and coppering of chlorophyllins. Both the 10,000-gallon mild steel hydrochloric acid storage tank and the 2000-gallon dilution tank have been lined with a vinyl-vinylidene polymer. Original acid handling lines, valves, and pumps were of hard rubber materials; however, replacements are constructed of copolymers of styrene and butadiene with acrylonitrile. There has been no penetration of acidification tanks during 2 years of operation, however severe corrosion and pitting have occurred in the $^{1}/_{4}$-inch wall of these vessels. Stainless steel construction in chlorophyllin finishing equipment eliminates corrosion problems and ensures a high purity product.

Broad Research Program and Consumer Confidence Hold Key to Future

Although the spectacular 1951–52 growth period when consumption increased from 200 to 10,000 pounds per month has passed, research activities plus more stable consumer acceptance now seem to offer a promising future for chlorophyll extraction.

The Lake Worth plant has prepared laboratory quantities of several chlorophyll derivatives for study by other researchers. Dilute acidification of a mixture of chlorophyll *a* and chlorophyll *b* produces a mixture of pheophytin *a* and pheophytin *b* in similar proportions. Magnesium is split from the center of the chlorophyll molecule yielding also a magnesium salt. Acidification of the pheophytin mixture with more concentrated hydrochloric acid (34%) produces pheophorbide *a* and pheophorbide *b* by splitting off the phytyl group. Saponification of a chlorophyll mixture followed by acidification with a strong acid splits off the phytyl, opens the carbocyclic ring adjacent to the phytyl group, and substitutes two hydrogens for the central magnesium, as shown in the reaction for chlorophyllin processing. Thus, chlorin e_6 and rhodin g_7, respectively, are produced from chlorophyll *a* and chlorophyll *b*. In addition to these compounds, laboratory quantities of their copper complexes have also been supplied for study. Strong and Cobb also cooperate closely with medical studies on the role of chlorophyll in promoting healing of wounds and ulcers. Work is also planned on the isolation of the components of commercial chlorophyllins with the aim of determining the effective deodorizing agents present and, if possible, their mechanism. Other studies aim to determine the effects of chlorophyllin on the respiratory metabolism of the living body.

Research projects are under way at Lake Worth and some work has been carried out by American Chlorophyll at the University of Florida on the utilization of other vegetation as a raw material source. Ramie leaves from the Everglades still offer promise.

Future process improvements have been planned. In cooperation with manufacturers, American Chlorophyll engineers have designed processing equipment for continuous extraction of chlorophyll and carotenoids from dehydrated alfalfa leaf meal or other dry leafy material. Equipment has been fabricated and is now at the Lake Worth plant. No schedule has been set for erection of the $150,000 installation which will increase capacity of extraction from the present 50 tons to over 100 tons per day. Only minor modifications will be required in separation, purification, and finishing steps to process the additional extract. Also being considered—installation of vacuum equipment for evaporating and concentrating the yellow hexane extract to increase carotene recovery.

Acknowledgment

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Processing Equipment

(1E) Blaw-Knox Co., Buflofak Equipment Division, Buffalo 11, N. Y., long tube vertical natural circulation evaporator.
(2E) Bowser, Inc., Fort Wayne 2, Ind., leaf filter.
(3E) Butler Zizinnia Corp., Buffalo, N. Y., spray dryer.
(4E) Oliver United Filters, Inc., Chicago 1, Ill., Sweetland pressure filter.
(5E) Sharpe & Flynn, Inc., Philadelphia, Pa., double-cone blender.
(6E) Sharples Corp., Philadelphia 40, Pa., supercentrifuge.
(7E) Schriver, T. & Co., Harrison, N. J., plate-and-frame filter press.
(8E) Sprout-Waldron Manufacturing Engineers, Muncy, Pa., hammer mill; pelletizer; pneumatic conveyor system.

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French Synthetic Detergents From Petroleum

GORDON C. INSKEEP, Associate Editor

in collaboration with

ALEX MUSSARD

Shell Saint-Gobain, Petit-Couronne, France

PRODUCTION of synthetic detergents is a relatively new branch of the French chemical industry. The first plant, located at Petit-Couronne, was completed by the Shell Saint-Gobain Co. in 1951. Today the unit is producing annually 25,000 metric tons of a secondary alkyl sulfate detergent called Teepol.

Design of the French plant was based on experience gained from earlier plants built by Shell in England (*10*) and Holland. In 1949, Shell joined forces with Saint-Gobain to form a joint enterprise for the production of petrochemicals in France. Saint-Gobain is one of France's oldest and largest producers of heavy chemicals. The Teepol plant was the first facility of the combine to be completed. Last year a second plant was completed near Marseilles for the production of acetone, methyl isobutyl ketone, and other solvents from propylene. Both petrochemical plants have been built adjacent to refineries of the Shell Berre Co.

Other important producers of synthetic detergents in France include Esso Standard and Sinnova. Esso produces some 20,000 tons (21% active matter) of alkyl aryl sulfonates each year from detergent alkylate. Sinnova has recently commissioned a fatty alcohol plant at Toulouse, and production is soon expected to reach 36,000 tons of derivative products per year.

In the five years from 1947 to 1952 consumption of synthetic detergents in the free world rose from 300,000 long tons (calculated as 21% active matter) to approximately 1,200,000 long tons. Luitez estimates that U. S. syndet consumption will reach 1,500,000 long tons, 72% of the total U. S. market, by 1960 (*14*). He estimates syndet consumption in the rest of the free world (excluding North America) will reach 1,000,000 long tons, 27% of the total detergent market, by 1960.

In the United States production of synthetic detergents has had its fastest growth. In 1953 for the first time sales of synthetic detergents outstripped the sale of soap (*18*). McCutcheon (*15*) gives a detailed tabulation of synthetic detergents produced in the United States. Synthetic detergents are now available in every large country of the world, but in no country other than the United States have the synthetic products yet outsold soap. It has been predicted that by 1975 petroleum raw materials will be used to produce 2,000,000 tons of synthetic detergents (*16*).

In the United Kingdom in 1953 one third of all soaps and detergents were synthetic products; 170,000 tons of a total of more than 500,000 tons of soaps and detergents were synthetic products in 1953. The United Kingdom, following the United States, is the second largest consumer of synthetic detergents in the world. The secondary alkyl sulfates have been made in England at Shell's Stanlow refinery since 1942. Ethylene oxide condensation products and alkyl aryl sulfonates are also being manufactured in Britain on a large scale (*20*)

Use of nonsoap detergents in the Netherlands jumped from 2% of the market in 1948 to 24% in 1952. Shell erected a small pilot plant for the manufacture of Teepol in Amsterdam in 1935. In 1949 a commercial scale Teepol plant was put into operation at Shell's Pernis refinery near Rotterdam.

Table I. Soap and Synthetic Detergent Production in France[a]

	Soap, Thous. Tons	Synthetic Detergents, Thous. Tons
1945	114	...
1946	162	...
1947	209	...
1948	250	...
1949	255	...
1950	281	...
1951	302	25
1952	265	50
1953	306	75
1954	...	100 (estd.)

[a] Source, Union des Industries Chimiques.

Important pioneering work in the field of synthetic detergents was done in Germany. Leading firms in the development were H. T. Böhme, A.-G., and IG Farbenindustrie (*3, 8*). Böhme produced the first group of commercial products in 1929—a series of butyl ricinoleic esters. In 1930, IG Farben marketed in Germany the Igepon A series which comprised fatty acid esters of hydroxyethanesulfonic acid (*8*). During World War II the main source of German synthetic detergents was the hydrocarbon produced by the Fischer-Tropsch synthesis. Probably the most noteworthy development was production of the Mersol detergents. These were obtained by treating a selected portion of the Kogasin fraction from the Fischer-Tropsch synthesis with sulfur dioxide and chlorine. At Leuna, now in East Germany, 50,000 tons of Mersol were made during the war. The Nekals, developed earlier, were produced by simultaneous alkylation and sulfonation of naphthalene and were used as textile wetting agents. Polymerized olefins, condensed with phenol and reacted with ethylene oxide, gave polyglycol ethers which could be used as such or sulfonated to give the Igepals and Alipals (*13*). The production of Igepon T, the taurine derived product, has been described in a previous article in this series (*11*) and by McCutcheon (*15*).

Various Anionic Detergents Can Be Produced from Petroleum Raw Materials

The bulk of synthetic detergents of the anionic type now being produced from petroleum fall into three main classes—alkyl aryl sulfonates, alkyl sulfonates, and secondary alkyl sulfates. In addition to these and less important commercially, a series of nonionics and cationics can be produced wholly or partly from petroleum.

The alkyl aryl sulfonates were among the first and have grown to be the major detergent products produced from petroleum today (*7*). Of the several members of this class, polypropylenebenzenesulfonate is now practically the exclusive active material used in both domestic and industrial products (*2*). The first alkyl aryl sulfonates produced in the United States were those which resulted from the sulfuric acid refining of kerosine, gas oil, and lubricating oils. They were originally noted for their nuisance value alone (*5*).

The first Keryl benzenesulfonates were produced in the early nineteen thirties. A highly acid-treated or solvent-refined material, boiling from 425° to 475° F. is the raw material. Kerosine is chlorinated at about 140° F. until 1.1 to 1.2 atoms of chlorine are added to each molecule of hydrocarbon. The Keryl chloride then reacts with an excess of benzene in the presence of aluminum chloride to give a Keryl benzene which is then further purified by distillation and then sulfonated (*6*).

The product structures available in this process are primarily determined by components in the paraffinic distillates used. The preferred predominance of relatively straight-chain alkyl groups may be obtained by combinations of selection of paraffin distillate sources and use of acid or solvent refining to enrich paraffinic components (*7*). Chief drawback of this type of synthetic detergent has been the strong kerosine odor which persists in the sulfonate after sulfonation and drying. In addition to the kerosine hydrocarbons, olefins having from 10 to 15 carbon atoms and the unsaturation near the end of the molecule may also be used as a starting material. The initial reaction is with benzene, using an acid catalyst, followed by sulfonation and then the reaction with caustic.

Major products of the alkyl aryl sulfonates are now based on the reaction products of benzene with propylene tetramer. Sulfonation of dodecylbenzene can be carried out with 98% sulfuric acid, fuming sulfuric acid, or a combination of the two. At least one plant in the United States is operating by continuous sulfonation with liquid sulfur trioxide (*18*).

Alkyl Sulfonates. Paraffin-rich petroleum stocks may be treated with sulfur dioxide and chlorine and then processed directly to the sulfonates. A highly acid-treated oil having a Saybolt Universal viscosity of 40 to 50 seconds 100° F. is preferred. The reaction is rapid at 200° F., using about 1.7 parts by weight of sulfur dioxide and 0.9 part by weight of chlorine for each part of paraffin.

The resulting hydrocarbon sulfonyl chloride is neutralized with sodium hydroxide and separated from the unreacted oil prior to drying. The detergent properties of the alkyl sulfonates approach those of the alkyl aryl sulfonates, but the commercial processing problems have placed these materials at an economic disadvantage.

Alkyl Sulfates. Secondary alkyl sulfates can be produced either from petroleum stocks from wax cracking or from shale oil feed stocks. Teepol is produced from the former. The direct sulfation of wax olefins has been almost entirely a European development pioneered by the Shell group. It has not been commercialized to any extent in the United States.

The process as applied to shale oil feed stocks has been described by Stewart and McNeill (*19*). The cracked petroleum feed stocks contain 60 to 75% olefins, while the shale oil feed stocks contain only 25 to 30% olefins. Sulfation takes place at

Sodium Hydroxide Is Received in Drums as Solid Caustic

Drums are up-ended over hot water nozzles and dissolved caustic is collected in tank below

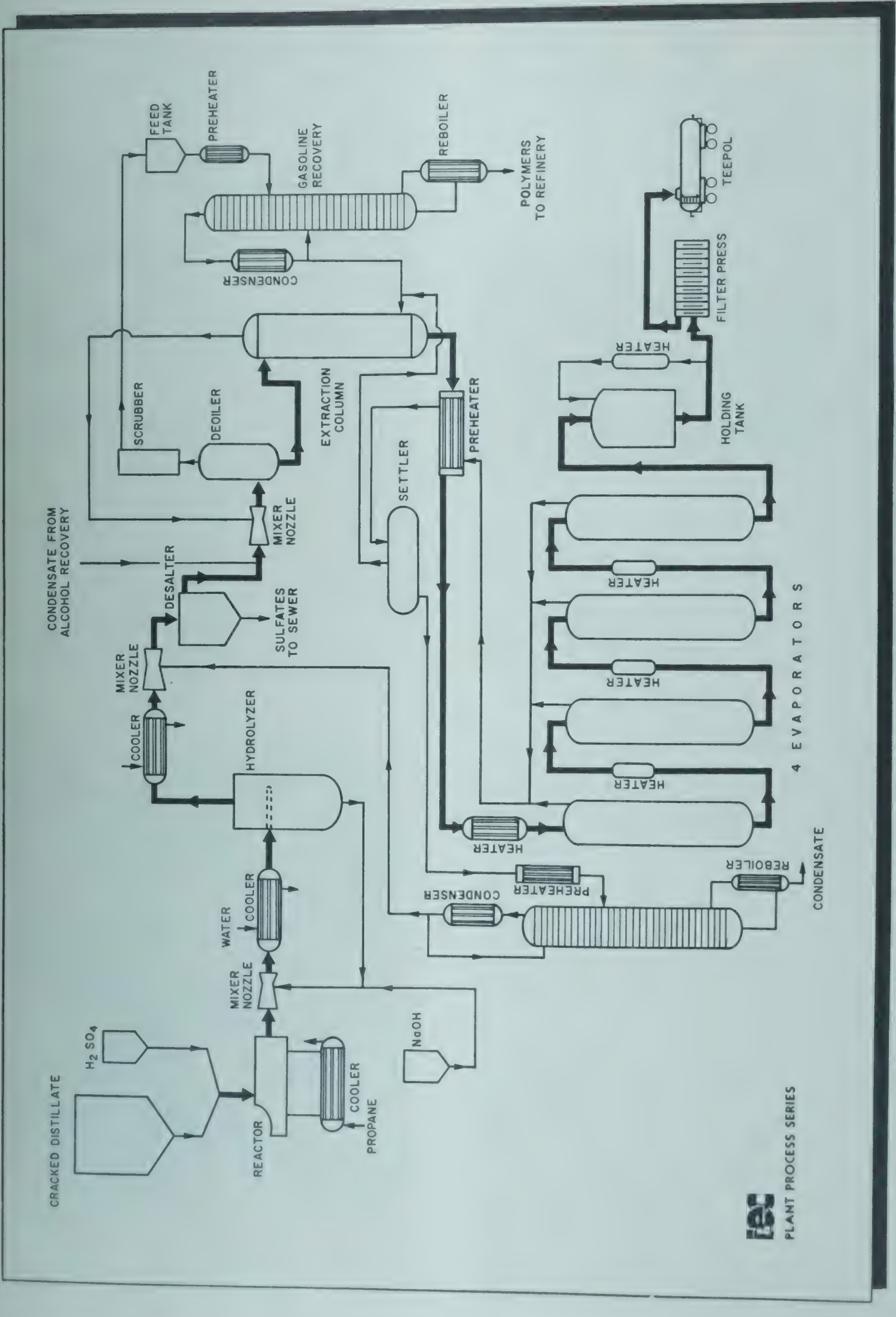
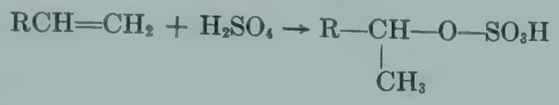

CRACKED DISTILLATE
H_2SO_4
REACTOR
COOLER
PROPANE
NaOH
MIXER NOZZLE
WATER
COOLER
HYDROLYZER
COOLER
MIXER NOZZLE
SULFATES TO SEWER
DESALTER
CONDENSATE FROM ALCOHOL RECOVERY
MIXER NOZZLE
DEOILER
SCRUBBER
EXTRACTION COLUMN
FEED TANK
PREHEATER
GASOLINE RECOVERY
CONDENSER
REBOILER
POLYMERS TO REFINERY
SETTLER
PREHEATER
HEATER
PREHEATER
CONDENSER
REBOILER
CONDENSATE
HEATER
HEATER
HEATER
4 EVAPORATORS
HOLDING TANK
HEATER
FILTER PRESS
TEEPOL
PLANT PROCESS SERIES

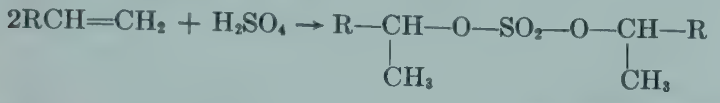
Figure 1. Flow Sheet for Production of Teepol at Shell Saint-Gobain Plant, Petit-Couronne, France

low temperature (Figure 2). Acid to olefin ratio is approximately 2 to 1. Critical operating conditions are efficient mixing and short contact time. An acid concentration of 90 to 96%, depending on feed stock, is used. The primary reaction is



$$RCH{=}CH_2 + H_2SO_4 \rightarrow R{-}\underset{\substack{|\\ CH_3}}{CH}{-}O{-}SO_3H$$

A secondary reaction also takes place



$$2RCH{=}CH_2 + H_2SO_4 \rightarrow R{-}\underset{\substack{|\\ CH_3}}{CH}{-}O{-}SO_2{-}O{-}\underset{\substack{|\\ CH_3}}{CH}{-}R$$

The bulk of the product consists of mono- and dialkyl sulfates with polymers and any unsulfatable materials originally present in the feed. Hydrolysis is generally carried out without separation of the mono- and dialkyl sulfates. When hydrolysis is complete the product is cooled, alcohol is added, and the hydrocarbons and higher alcohols are extracted with a suitable hydrocarbon solvent. A desalting operation may be included in the process to remove sodium sulfate.

In general, the primary sulfates possess markedly greater resistance to hydrolysis and better detergent properties than corresponding secondary derivatives (*1*). Much effort has been directed toward the development of methods of production of these types of synthetic detergents from petroleum hydrocarbons.

Teepol Is Based on Cracked Petroleum Wax Which Is Sulfated and Neutralized

Refining of lubricating oil yields large quantities of paraffinic waxes which, when cracked under carefully controlled conditions, produce a mixture of olefins; these in turn may be sulfated, and neutralization of the resulting alkyl sulfuric acid yields a product possessing valuable detergent characteristics. The obvious factors that might influence the properties of the end product are:

1. Normal or branched nature of the carbon chain
2. Length of the chain
3. Position of the sulfate group
4. Nature of the cation

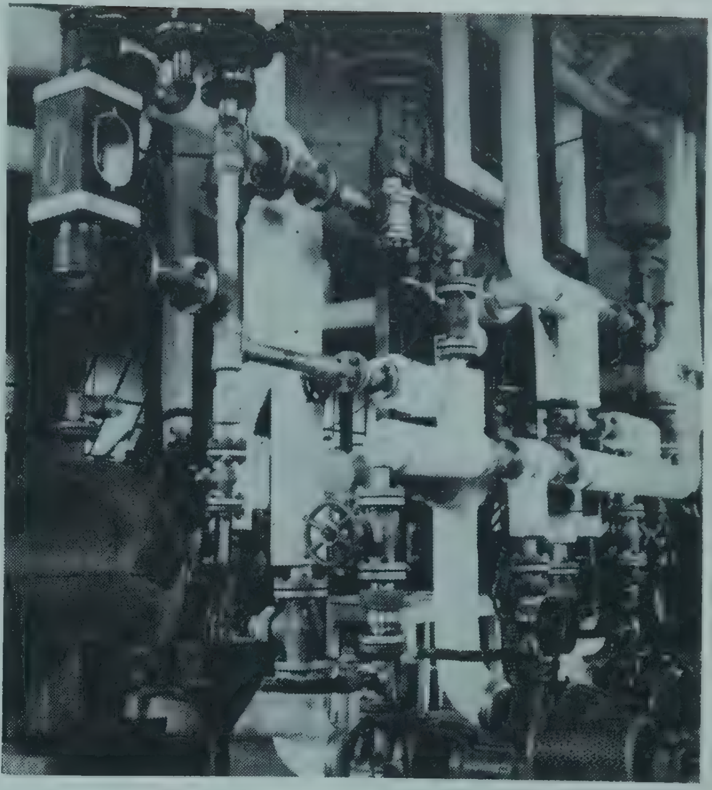
Shell research laboratories investigated these factors for their specific effect on wetting power, foaming and emulsifying ability, thermal stability of pure product and of solutions, and solubility. It was found that molecules of Teepol with normal carbon chains have the best detergency and that the length of the carbon chain should be between 8 and 18 carbon atoms—the same range as found in soaps and the fatty acids derived from coconut oil which form the organic raw material of many synthetic detergents.

The position of the sulfate group (largely determined by that of the double bond in the original olefin) should preferably be on the second carbon atom; however, foaming ability is promoted when the sulfate is near the middle of the chain so that some olefin with the double bond removed from the end of the chain is not objectionable.

The nature of the cation is of less marked influence. Sodium hydroxide has many advantages as a neutralizing agent, but for special applications the use of other alkalies—for example, ammonia and triethanolamine—has been investigated.

Therefore, the organic substrate chosen for the manufacture of the normal grade of Teepol is a C_8 to C_{18} fraction from cracked paraffins, termed "cracked distillate," with high content of normal α-olefins.

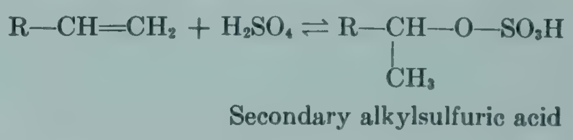
Treatment of olefins with sulfuric acid will cause a variety of reactions. According to the conditions used, there may be formed monoalkylsulfuric acid, dialkylsulfate, sulfonic acid, alcohol, sulfur dioxide, and sulfones; isomerization may also occur and the end product under vigorous conditions will be polymers (*17*).



Reaction and Neutralization Section of Teepol Plant

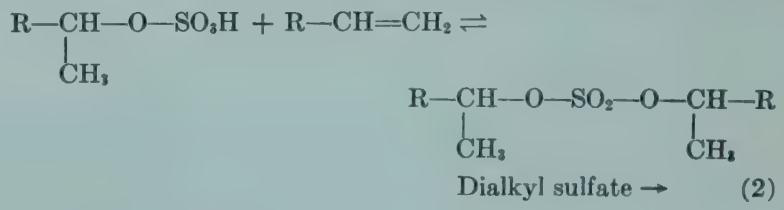
Guarded pump drive shafts, shielded rotameter, and air-actuated valves are in view

The following set of reactions may be assumed:



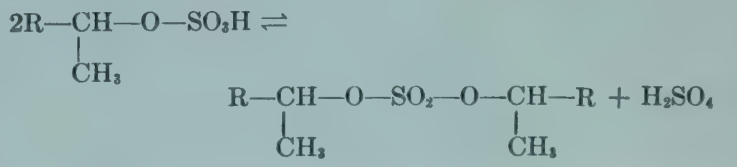
$$R{-}CH{=}CH_2 + H_2SO_4 \rightleftharpoons R{-}\underset{\substack{|\\ CH_3}}{CH}{-}O{-}SO_3H$$

Secondary alkylsulfuric acid (1)

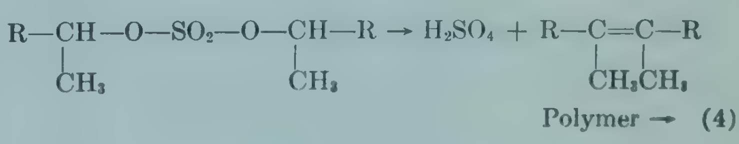


$$R{-}\underset{\substack{|\\ CH_3}}{CH}{-}O{-}SO_3H + R{-}CH{=}CH_2 \rightleftharpoons R{-}\underset{\substack{|\\ CH_3}}{CH}{-}O{-}SO_2{-}O{-}\underset{\substack{|\\ CH_3}}{CH}{-}R$$

Dialkyl sulfate → (2)

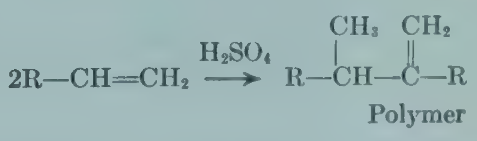


$$2R{-}\underset{\substack{|\\ CH_3}}{CH}{-}O{-}SO_3H \rightleftharpoons R{-}\underset{\substack{|\\ CH_3}}{CH}{-}O{-}SO_2{-}O{-}\underset{\substack{|\\ CH_3}}{CH}{-}R + H_2SO_4 \quad (3)$$



$$R{-}\underset{\substack{|\\ CH_3}}{CH}{-}O{-}SO_2{-}O{-}\underset{\substack{|\\ CH_3}}{CH}{-}R \rightarrow H_2SO_4 + R{-}\underset{\substack{|\\ CH_3}}{C}{=}\underset{\substack{|\\ CH_3}}{C}{-}R$$

Polymer → (4)



$$2R{-}CH{=}CH_2 \xrightarrow{H_2SO_4} R{-}\overset{\substack{CH_3\\ |}}{CH}{-}\overset{\substack{CH_2\\ \|}}{C}{-}R$$

Polymer (5)

This mechanism is partly substantiated by the observed reaction rates and serves to indicate that if polymerization is to be avoided, the conditions chosen should not be too drastic, particularly temperature, acid concentration, and reaction time. However, it gives no insight into the real mechanism of the process, nor does it account for the formation of side products, such as sulfonic acid, sulfones, and sulfur dioxide, which appear to be favored by high acid concentration and long reaction time.

The experimental results can largely be explained in terms of a reaction system involving the formation of carbenium (often inappropriately termed "carbonium") complexes (*21*). Using a 1-alkene as an example, the following reactions might be expected:

$$R-CH=CH_2 + H_2SO_4 \rightleftharpoons \underset{\text{I}}{(R-CH-CH_3)^+ HSO_4^-} \qquad (1)$$

As written, the complex would be unstable (R being aliphatic), and stabilization by solvation would occur

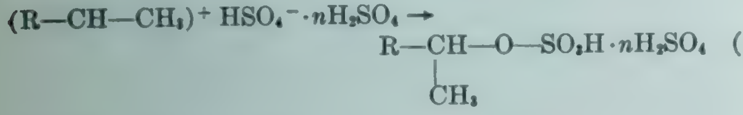
$$(R-CH-CH_3)^+ HSO_4^- + nH_2SO_4 \rightleftharpoons (R-CH-CH_3)^+HSO_4^-\cdot nH_2SO_4 \qquad (2)$$

Upon decomposition, the carbenium complex will form in part a 2-alkene

$$(R-CH-CH_3)^+ HSO_4^-\cdot nH_2SO_4 \rightleftharpoons R'-CH=CH-CH_3 + (n + 1)H_2SO_4 \qquad (3)$$

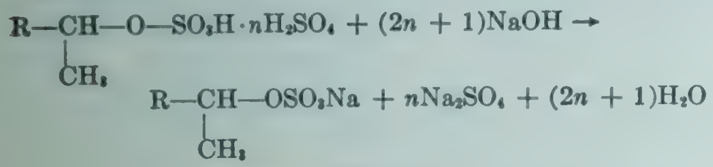
However, this does not affect the final equilibrium, since the addition of sulfuric acid to a 2-alkene preferentially forms the original carbenium complex, I.

Under mild conditions, the main reaction is:



$$(R-CH-CH_3)^+ HSO_4^-\cdot nH_2SO_4 \rightarrow R-\underset{\substack{|\\CH_3}}{CH}-O-SO_3H\cdot nH_2SO_4 \qquad (4)$$

Followed by neutralization:



$$R-\underset{\substack{|\\CH_3}}{CH}-O-SO_3H\cdot nH_2SO_4 + (2n + 1)NaOH \rightarrow R-\underset{\substack{|\\CH_3}}{CH}-OSO_3Na + nNa_2SO_4 + (2n + 1)H_2O$$

Teepol (5)

Competing side reactions lead to (*a*) formation of dialkyl sulfate which can be interpreted as a stabilization of the carbenium complex, (*b*) isomerization, and (*c*) formation of non-β-alkyl sulfates. Finally, polymerization can be presumed to involve the reaction of the carbenium complex with an olefin or of two carbenium complexes.

In plant operation, the variables which are found to have a predominant effect on the yield of the reaction and the quality of the end product are:

1. Quality of the base stock
2. Acid concentration
3. Acid to olefin ratio
4. Reaction time and temperature

Other variables, such as reactor design, degree of mixing, neutralization and hydrolysis conditions, also affect the quality of the product.

French Plant Receives Utilities from Adjacent Refinery; Raw Materials by Water, Rail, and Road

Shell Saint-Gobain has erected its Teepol plant immediately adjacent to the Shell Berre refinery at Petit-Couronne, near Rouen, France. By agreement with Shell Berre all utilities with the exception of compressed air are supplied by the refinery. The refinery is also responsible for maintenance and security and assists in the administrative work. The Teepol plant covers an area of approximately 5$^1/_2$ acres.

Cracked distillate is shipped from the Shell refinery near Rotterdam by sea tanker to unloading docks at Petit-Couronne. It is stored there in 300,000-gallon storage tanks. Sulfuric acid is delivered by railroad tank car or by tank wagon from one of the large Saint-Gobain plants and pumped (*7A*) from the tank cars to a 30,000-gallon storage tank. Sodium hydroxide is received in drums as solid caustic. It is dissolved with hot water in special open tanks from which it is pumped to two 7500-gallon storage tanks. The caustic is diluted and stored at process concentration.

The cracked distillate and sulfuric acid are fed into the reactors (Figure 1) by centrifugal pumps; the flow rates are indicated by rotameters (*11A*). In normal operations 22 tons per day of cracked distillate is used. There are three reactors available, but only two are used simultaneously. Reactants are thoroughly

General View of Teepol Plant

Much of the processing equipment is out of doors; control room of brick and glass (right) gives operator unobstructed view of equipment; towers are for extraction and solvent recovery mixed in a centrifugal pump (*6A*), driven by electric motors. Temperature is controlled by a shell-and-tube heat exchanger. Liquid propane is used as coolant. The reaction temperature as well as the residence time can be varied and depends on the grade of Teepol to be manufactured. Variations in the reaction conditions are based on an on-the-spot titration of the free acid remaining in the reaction mixture.

Neutralization and Hydrolysis. The dark-colored mixture from the reactor flows to a nozzle, where it is mixed with caustic solution. The caustic solution is fresh product diluted with product drawn from the bottom of the neutralizing vessel. The neutralization mixture passes through a shell-and-tube cooler, the temperature being controlled by a flow of water. The mixture then enters the hydrolyzer through a perforated U-tube which acts as a distributor.

Complete neutralization takes place, and conditions in the vessel are such as to cause hydrolysis of the dialkyl sulfates. Control over this part of the process is by titration of the product at outlets of the mixing nozzle and the neutralizing vessel.

The product leaving the hydrolyzer is cooled and mixed with alcohol in another mixing nozzle. The alcohol acts as a desalting agent. The mixture flows to a large decanter from which the sulfate brine is drawn off at the bottom and the product flows through a line placed roughly two thirds up the vessel. Both outlet valves are controlled automatically by means of level controllers. Temperature of the product during desalting operations varies between 50° and 60° C.

The alcoholic product leaving the desalter is diluted with condensate (available from the alcohol recovery column) and then purified in a liquid-liquid extraction process, using gasoline. The gasoline removes all unsulfated organic material.

The first stage in the process is a mixing of the combined alcoholic product and condensate with gasoline from the top of the extraction column and then separating the two phases in a de-oiler. The gasoline-containing layer leaves the de-oiler through a scrubber, placed on top of the de-oiler, and flows by gravity to a tank from which it is then distilled.

The layer containing the active matter is pumped from the bottom of the de-oiler to the top of the extraction column. It flows down the column while gasoline is pumped into the bottom of the column. The active matter leaves the bottom of the column and flows to an evaporator feed tank.

Evaporation. The active Teepol is then concentrated in a four-stage evaporation system, with interstage heat exchangers. The Teepol is flashed into the evaporator through conical sprayers which have been empirically designed to prevent foaming. The evaporators (*10A*) are insulated, cylindrical vessels; the first two vessels have capacity of 1500 gallons and the last two, 1000 gallons.

Alcohol, gasoline, and water are evaporated, and the concentrated Teepol is pumped from the bottom of the last evaporator. The temperature in this stage of the process increases stepwise from the first to the fourth evaporator, to a high point of 100° C.

Table II. Utilities Requirements

(To produce 1 metric ton Teepol at 21% active matter content)

Steam (high pressure), lb.	200
Steam (low pressure), lb.	2,000
Water, U. S. gal.	22,000
Electricity, kw.-hr.	45

Finishing. Teepol, on leaving the evaporators, is pumped (*9A*) into one of the two 8000-gallon holding tanks. An analysis of the product is taken at this time before it is pumped to a finishing and storage tank. There are four finishing tanks, each with a capacity of 198,000 gallons. While the finishing process is under way, the contents of these tanks is continuously recycled through a shell-and-tube heat exchanger and the temperature held at 33° C. This makes subsequent filtration easier, and mixing is enhanced by means of a jet fitted in the tank inlet.

The active matter content, pH, and alkalinity of each storage tank must be adjusted to the sales specification of the particular product; however, the main finishing operation is filtration from impurities. Plate-and-frame filter presses (*4A*) are used with diatomaceous earth as a filter aid. A suspension of filter aid in a limited amount of Teepol is pumped through the filters over and over again until the cloths are thoroughly precoated.

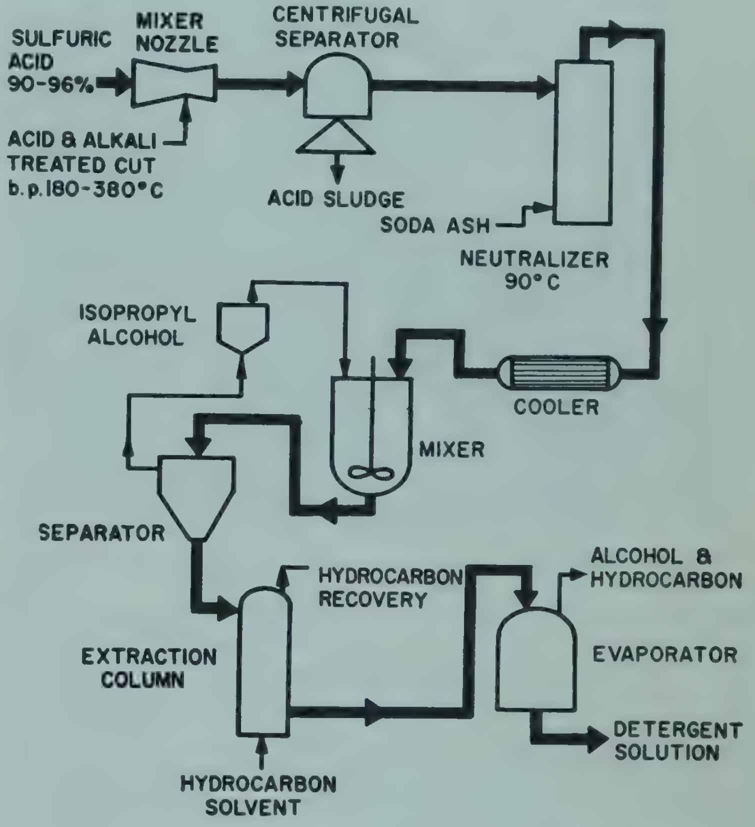


Figure 2. Alkyl Sulfates from Shale Oil

Tank cars, drums, or barrels are filled by gravity (*3A*) from the filling tanks, which are located on an elevated concrete platform. Scales (*8A*) are used to measure the quantity filled into each container. All the drums or barrels are handled by fork truck (*1A*).

Shipments from the plant are made in tank barges, tank cars, 50-gallon drums, or 40-gallon barrels. Teepol is packed in smaller containers at various distribution centers.

Solvent Recovery. The alcohol and gasoline vapors from the evaporators, after giving up heat to the raffinate entering the first evaporator, are condensed and then separated in a settler. The upper layer, combined with the product from the gasoline recovery column, is used as feed for the extraction column (Figure 2).

The bottom layer is fractionated in a conventional bubble-cap column. The bottoms from the column, mainly water, are used as recycle condensate. Any excess goes to the sewer.

Extract from the de-oiler goes through the scrubber to the gasoline recovery column, after being heated in a shell-and-tube heat exchanger. Recycled gasoline leaves the column from the top, while the unsulfated organic matter is withdrawn from the bottom of the reboiler. These polymers are pumped to the adjacent Shell Berre refinery where they are utilized as valuable reforming stock.

French Plant Is First Teepol Unit Designed for Completely Automatic Control

The Petit-Couronne plant is the first Teepol plant to be designed for completely automatic control. Extensive use of in-

Four-Stage Evaporation System

Detergent is flashed in evaporator through conical sprayers, empirically designed to prevent foaming

struments has made it possible to limit the operating personnel to 28. The plant operates on a 24-hour basis, and the men work six 8-hour shifts each week. Four shifts have been set up; while three of the shifts alternate, one shift is off or is available for maintenance work.

Two electrically driven compressors (*2A*) are located in the pump house. These deliver air at 55 pounds per square inch gage which is stored in two receivers. One of the receivers is used for instrument air supply, which is furnished through a reducing valve at 17.5 pounds per square inch gage.

In addition to the instrumentation outlined in Table III, a number of pressure recorder-controllers, flow indicators, level alarms, and level gages, together with pressure alarms and temperature recording instruments, have been installed in a central control room. An electronic multiple-point instantaneous temperature indicator and a galvanometer multiple-point strip chart temperature recorder (*5B*) are also in the control room. After an initial adjustment period the Teepol plant has operated quite smoothly on full instrumentation. The average operational efficiency is higher than in the similar plant manually operated.

Carbon Steel Used Extensively in Most of Teepol Plant

Carbon steel (A.S.T.M. Code A, 285 grade C.) is generally used throughout the Teepol plant. However, since a detergent solution can be quite corrosive at elevated temperatures, special materials are used in the evaporation section (Table IV). This is also true in part of the solvent recovery installation. An 18-8 stainless steel has been found quite satisfactory. As an additional protection against corrosion, ammonia is injected into the vapor line of the solvent recovery distillation column.

In order to prevent rust formation in the larger Teepol finishing tanks, an asphalt coating was applied over ordinary carbon steel instead of using expensive materials. The finished product is stored in aluminum vessels in order to avoid any corrosion, which might reintroduce undesirable metallic ions.

Special alloys, such as aluminum bronze and Monel, are used in the few sections where corrosion and erosion are particularly severe. Entrance of the reaction product to the neutralization nozzle is through an injection fitting; at this point only Teflon has been found entirely satisfactory. The glass tubes of the rotameters which measure strong caustic solutions are attacked and must be renewed frequently.

Centrifugal pumps used in the plant are all, with the exception of those handling sulfuric acid, caustic, and gasoline, fitted with mechanical seals (*5A*), instead of the usual stuffing boxes. The mechanical seals have stood up well in operation.

Teepol Production Is under Constant Chemical Control

The value of the products being processed and the danger of contamination of the circuit make a constant chemical control of production imperative. For this reason as many as 15 of the 70 men working in the Teepol plant are employed in the laboratory. Eight of these are working on three 8-hour shifts.

The principal raw materials (cracked distillate, sulfuric acid, alcohol, and gasoline) are checked every time a shipment is received. Caustic and diatomaceous filter aid are not analyzed in a systematic manner, but only on special request of the receiving department or if some unsuspected problem that arises in production might be traceable to the raw materials involved. The most frequent tests are outlined in Table V.

For rapid adjustment of the sulfation reaction, a sample of the product leaving the reactors and two further samples, one taken after the product-caustic mixer and the other at the outlet of the neutralizing vessel, are titrated once every hour. The titration is done in the process building by the operator on duty.

General Safety Rules for the Oil Refinery Apply in Teepol Plant

Plant buildings are of fireproof construction, and operating temperatures are such that no important fire hazard is encountered. However, highly flammable products, such as cracked distillate, alcohol, and gasoline, must be considered. Since the Teepol plant is located within the refinery area, all general safety rules valid in the refinery apply.

Smoking is prohibited. All metal apparatus is grounded, and no work requiring an open flame may be undertaken without the written approval of the plant superintendent, of the head of the fire department, and of the director of the refinery or his

Table III. Instrumentation

Conditions Controlled	Instrument	Location
Feed rates of acid and olefin	Ratio flow controllers	Reactor feed lines
Reaction temperature	Pressure controller	Propane line to reactor heat exchanger
Feed ratio of gasoline to crude Teepol solution	Ratio flow controllers (*1B*)	Extraction column feed lines
Liquid level in gasoline extraction column	Level indicator-controller (*3B*)	Extraction column product lines
Flow of raffinate to evaporators	Flow recorder-controller	Feed line to first evaporator
Liquid level in evaporators	Level controller coupled to automatic valves (*6B*)	Outlet lines from each evaporator
Feed rate to gasoline recovery column	Flow recorder-controller	Extract feed line
Gasoline distillation pressure	Pressure recorder-controller (*4B*)	Gasoline recovery column vapor line
Gasoline distillation temperature	Temperature controller (*8B*)	Steam feed line to reboiler
Level on gasoline recovery column	Level controller (*7B*)	Outlet line from reboiler

Table IV. Materials of Construction

Product or Operation	Equipment	Material
Neutralization	Mixing nozzle	A.S.T.M Code B 148-46 T and Monel; Teflon injection fitting
Evaporation	Evaporator	A.S.T.M. A 176-44, Type 410
Teepol storage and finishing	Tanks	Steel with special asphalt lining
Teepol	Filling tanks	A.S.T.M. B 209-46 T, Grade I aluminum

delegate. All lighting is of the vaporproof type, and all motors within enclosed areas are of the explosionproof type. All drive shafts are enclosed in rigid guards.

Fire extinguishers, including foam and carbon dioxide types, are available in the pump house, process building, laboratory, and workshop. All tanks except those containing Teepol are surrounded by the usual concrete dykes. Tanks containing highly flammable materials are equipped with foam injection lines and water sprays. Four water hydrants are located at strategic points. These hydrants would be used by the mobile fire-fighting units of the refinery's fire brigade in case of emergency.

Goggles and acid- and alkali-resisting gloves and clothing are provided for any operations in contact with these corrosive agents. Acid and caustic rotameters are protected by special plastic covers. First aid cabinets and tubs containing neutralizing solutions are located in the pump house and in the process building. An infirmary, equipped with stretcher, first aid supplies, and a bed, is located next to the workers' locker room.

The Petit-Couronne plant has set up an enviable safety record. To date no serious fire has occurred, and the refinery fire brigade has never been alerted. Cases requiring medical attention with interruption of work (primarily minor cuts, bruises, and burns) have averaged only six per year.

Greatest Volume of Product Goes into Liquid Household Detergents

Although Teepol is produced only in Holland, England, and France, it is available in all countries where there are Shell companies. Grades commonly sold are Teepol 410, which contains 20 to 22% active material, and a slightly more concentrated product, Teepol 610. It is also available in other concentrations up to Teepol 710, which contains 40% active material.

In France and in most countries the largest volume of Teepol is sold to formulators for preparation of liquid household detergents. The approximate over-all sales pattern today: 50% for liquid household detergents; 20% for industrial cleaning agents; and 30% for miscellaneous industrial uses.

Shipments from Plant Are Made in Barrels, Drums, Tank Barges, and Tank Cars

Control Laboratory

Close analytical control is maintained on production on 24-hour basis

The synthetic liquid detergents appeared in Europe shortly after World War II as substitutes for solid soap products which were in short supply. The liquid detergents did not become universally popular at that time, primarily because of shortages of suitable packing materials and lack of an adequate sales promotion campaign.

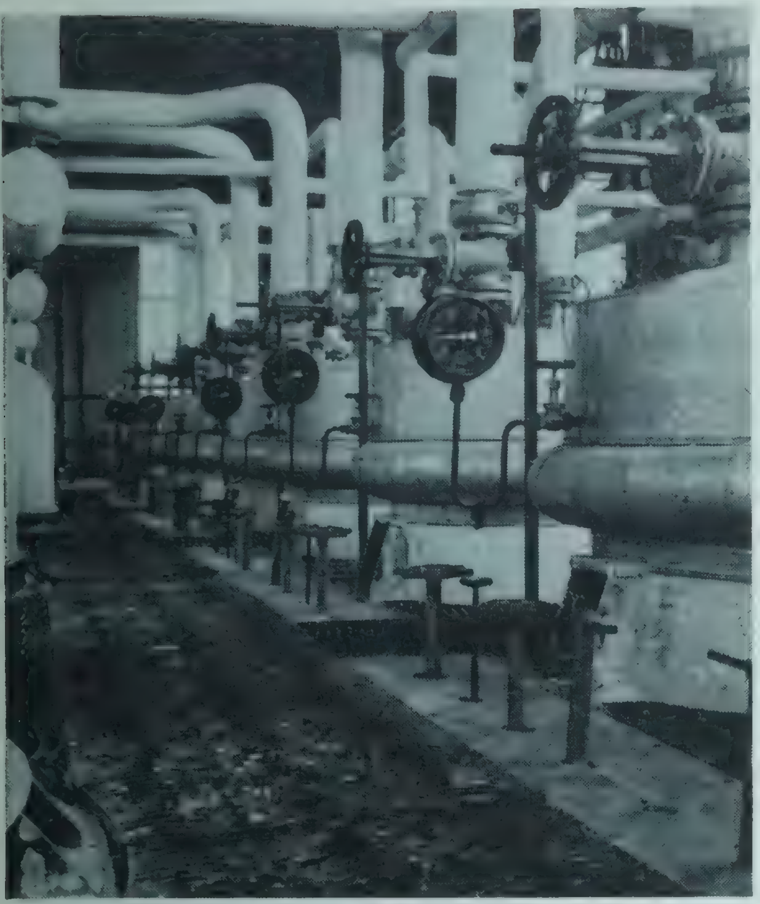
Today, well-designed dispensing type bottles, attractively labeled, have boosted the sales appeal of liquid detergents. Holland and Belgium are each using over 40,000,000 bottles a year. Similar sales records have been established in Britain and France. A large proportion of these bottled products are based on Teepol. Outstanding advantage of an alkyl sulfate type detergent for liquid products is its high solubility in water.

Table V. Analyses of Raw Materials

Product	Analysis
Cracked distillate	A.S.T.M. distillation; flash point; density
Sulfuric acid	Concentration
Sodium hydroxide	Iron and alumina content
Gasoline	Distillation range
Alcohol	Density

In addition to its use as a liquid household detergent, Teepol is also widely used as an industrial detergent in laundries and in public buildings. Liquid syndets are ideally suited for laundries equipped with automatic control in view of their high degree of solubility, ease of handling, and nonformation of insoluble calcium and magnesium salts (*4*).

There are a number of applications in the textile field. For scouring raw wool, Teepol has the marked advantage of not requiring soft water and of retaining high activity in a neutral medium. Electrolytes such as sodium chloride enhance its detergency. Many finishing processes for cotton utilize a wetting agent—for example, the urea-formaldehyde anticrease process. Teepol is stable to most of the chemicals used in these finishing



Heat Exchangers Operating between Stages of Final Evaporation Operation

processses and is therefore widely used in the various scouring processes.

Teepol is compatible with dyestuffs of almost all classifications, with the exception of the basic dyestuffs and fast-color salts which are used in the production of azoic colors. The prime function of Teepol in dyeing is to reduce surface tension of the dye color, thereby ensuring quick wetting and good penetration of the dye liquor.

Hill (*9*) has described the use of a wetting agent, such as Teepol, and calcium chloride for consolidation of dust deposited on mine roadways. Teepol has also been used as a wetting agent for zinc dust in the cyanide process for extracting gold from gold-bearing rock. In other mining operations, dust at the cutting face has been easily reduced by addition of small amounts of Teepol into the water spray.

Expanded European Market Predicted for Liquid Detergents

While new industrial uses are being developed which will demand increasing volumes of Teepol, the real future market of the product seems to be in the field of household liquid detergents. In Europe, this type detergent is increasing in popularity, and its share of the total soap and synthetic detergent market is expected to increase in future years.

Research is continuing in an effort to improve the Teepol manufacturing process. The successful operating record of the Petit-Couronne plant has established the value of a completely instrumented unit. Any future Teepol plant would undoubtedly be designed for this type or even more complete automatic control.

One of the steps in the process that has received considerable attention is the initial reaction of acid and olefin. Various types of contacting devices have been designed in the Shell laboratories in Amsterdam (*12*). The objective is to improve temperature control and raise the yield.

The synthetic detergent industry in France is just getting a start, but if it follows the American pattern, it has indeed a bright future.

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Processing Equipment

(1A) Clark Equip. Co., Battlecreek, Mich., Yardlift 4024 and F.E.N. (France) Salev 253PE.
(2A) Crépelle et Cie., Lille, France, Model EM.00.S, air compressors.
(3A) Emco Brass Mfg. Co., Croydon, England, Model B 291 loading assembly.
(4A) Filtres Philippe, Paris, France, Model AP.4 SC (aluminum alloy), filter press.
(5A) Flexibox, Manchester, England, Models RRCQ and RTC mechanical seals.
(6A) N. V. Koninklijke Nederlandsche Machinefabriek, Helmond, Holland, centrifugal pumps.
(7A) Rheinhütte, Wiesbaden, Germany, Model RE 50/80/235, sulfuric acid pumps.
(8A) S.A. de Construction de Voiron (France) and Etabl. Testut, Paris (France), platform scales.
(9A) Model KNA-2a, Sigmund Pumps, Ltd., Gateshead (England).
(10A) Soc. des Forges et Ateliers du Creusot, le Creusot (France), evaporators.
(11A) Soc. Otic-Fischer, Clermont-Ferrand (France), under Fischer-Porter licence, rotameters.

Instruments

(1B) Fischer & Porter Co., Hatboro, Pa., Flowrator with Foxboro pneumatic receiver and Stabilog valve.
(2B) *Ibid.*, Flowrator with Mason-Neilan automatic valve.
(3B) Foxboro Co., Foxboro, Mass., differential type D.P. cell, with Foxboro Stabilog indicator controller and Stabilflo valve.
(4B) *Ibid.*, Stabilog with Stabilflo valve.
(5B) Leeds and Northrup, Philadelphia 44, Pa., Speedmax 6-point potentiometer recorder and 24-point potentiometer indicator.
(6B) Mason-Neilan Regulator Co., Boston 24, Mass., No. 12, 601-15 with automatic valve.
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(8B) Taylor Instrument Co., Rochester 1, N. Y., self-acting temperature controller with Stabilflo valve.

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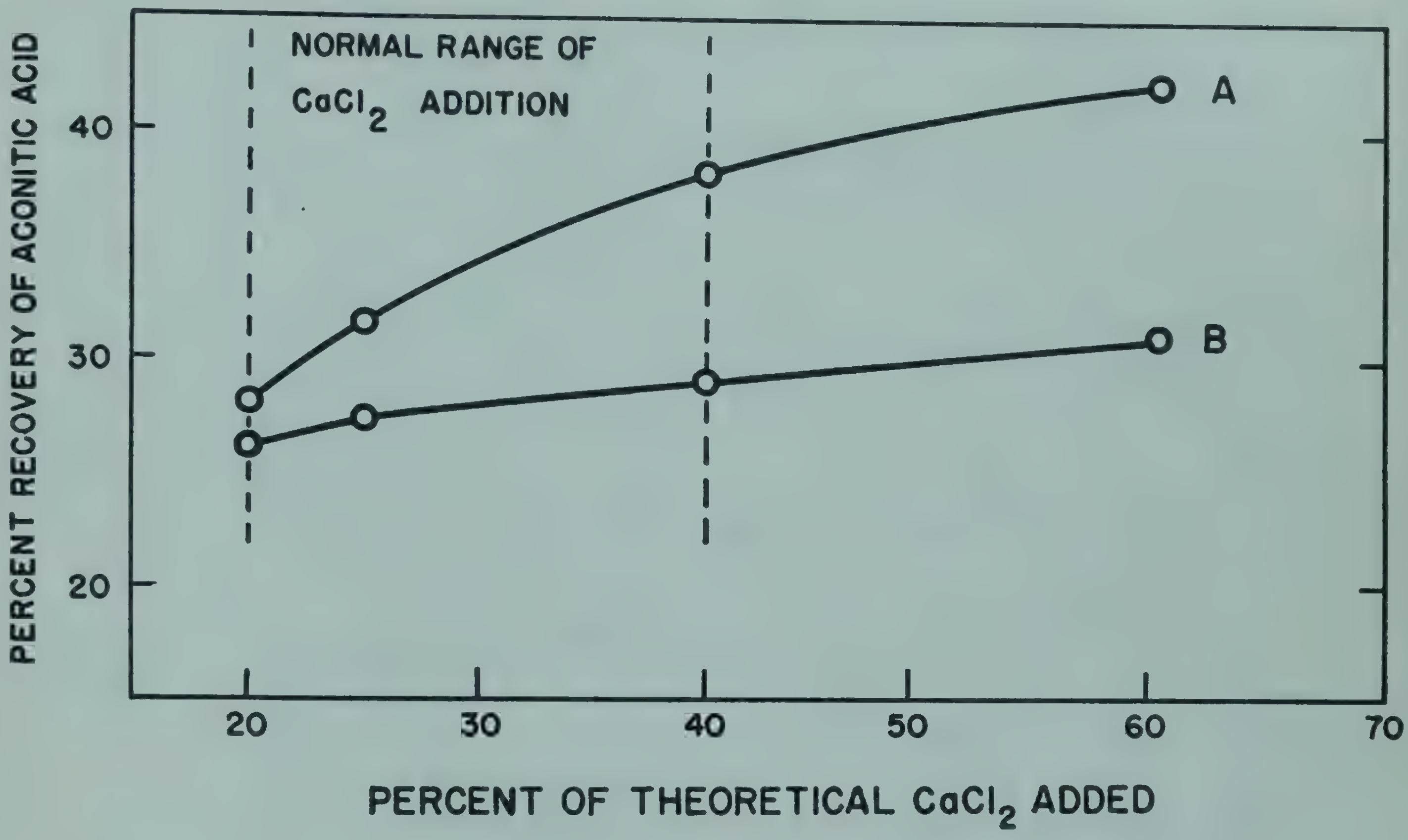
Determining Economical Aconitic Acid Recovery From Molasses



(A) Higher $CaCl_2$ makes aconitic acid recovery feasible with this type of molasses.

(B) Aconitic acid recovery is uneconomical with this type of molasses.

Calcium Magnesium Aconitate

HARRY W. HAINES, JR., Associate Editor
in collaboration with
LESLIE G. JOYNER
Godchaux Sugars, Inc., New Orleans, La.

ACONITIC acid, until recently, was produced only in small amounts as an expensive dehydration product of citric acid (*5, 9, 27*), even though it is the principal organic acid in cane juice, exclusive of amino acids (*6, 7, 21, 30*). During the processes of sugar manufacture, aconitic acid salts remain in solution when the sugar is crystallized, and these aconitates accumulate in the molasses. Behr (*8*) first noted in 1877 that aconitic acid was a component of sugarhouse products. However, it was not separated until the Iberia Sugar Cooperative, Inc., in New Iberia, La., demonstrated in 1944 and 1945 that alkaline-earth aconitates may be recovered in commercial quantities from second or "B" molasses (*19, 25, 26*). They found that molasses, after aconitate removal, could be used in the sugarhouse without requiring alterations of any of the processes usually employed for sugar recovery.

The world's sole producer of dicalcium magnesium aconitate is Godchaux Sugars, Inc., at Raceland, La. The company employs a process originally developed by the Southern Regional Research Laboratory, Southern Utilization Research Branch of the U. S. Department of Agriculture (*3, 4, 14, 17, 28, 29*). Production of this salt in commercial quantities has opened many new possibilities for utilizing aconitic acid and its esters. Every year at least 4,000,000 to 5,000,000 pounds of aconitic acid are potentially recoverable in this manner from sugar cane grown and milled in Louisiana and Florida. Louisiana cane is best suited for aconitate production because of its high acid content, which varies between 0.1 and 0.2% (3 to 7% based on dry solids in the molasses). High acid content is apparently due to the short growing season in subtropical areas. While most of the Louisiana molasses averages about 5% aconitic acid, on a dry solids basis, none containing less than 3% can be processed economically.

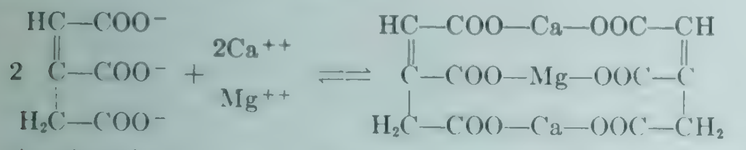
One of the principal uses for aconitic acid is in the production of high molecular weight esters which are used as plasticizers (*10, 13, 16, 20, 24*). The most common plasticizer is tributyl aconitate; other important ones include triamyl aconitate, triallyl aconitate, and tri(2-ethylhexyl) aconitate.

In the past Godchaux has supplied various customers with calcium magnesium aconitate, which is converted to the free acid or its esters. In effect, the aconitate plant contains a railroad in its unit operations for transportation of calcium ions, because Godchaux buys the calcium chloride used in aconitate production from one of its purchasers of calcium magnesium aconitate.

Equally novel among Godchaux operations is the "in transit" processing of raw materials. The Raceland plant uses B molasses from its own sugar factory during the cane grinding period, which in Louisiana extends from mid-October through December. During the nongrinding season, the plant processes blackstrap molasses from other mills. Treated molasses from Raceland finally reaches the customer, although it may have originated from a mill in another part of the state.

Chemistry of process has been well defined

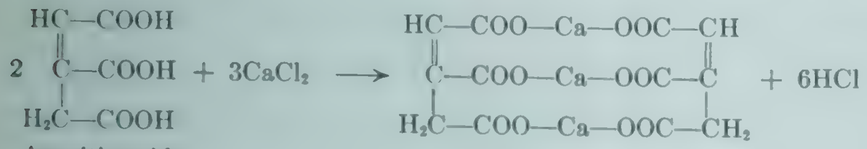
Fundamentally, the production of dicalcium magnesium aconitate involves very simple chemistry (*17, 18*), coupled with the necessary unit operations to effect recovery. Molasses usually contains some calcium ions, so that it is necessary only to make up the deficiency needed for precipitation of aconitic acid. There is no need for additional magnesium; molasses normally contains a sufficient quantity of these ions.



$$2\ \begin{array}{l}\text{HC—COO}^-\\ \ \|\\ \text{C—COO}^-\\ \ |\\ \text{H}_2\text{C—COO}^-\end{array} + \begin{array}{c}2\text{Ca}^{++}\\ \\ \text{Mg}^{++}\end{array} \rightleftharpoons \begin{array}{l}\text{HC—COO—Ca—OOC—CH}\\ \ \|\qquad\qquad\qquad\qquad\ \|\\ \text{C—COO—Mg—OOC—C}\\ \ |\qquad\qquad\qquad\qquad\ |\\ \text{H}_2\text{C—COO—Ca—OOC—CH}_2\end{array}$$

Aconitate ion Dicalcium monomagnesium aconitate

The amount of calcium added depends on the type of molasses, but is generally within the range of 20 to 40% of the theoretical quantity needed to precipitate the tricalcium salt



$$2\ \begin{array}{l}\text{HC—COOH}\\ \ \|\\ \text{C—COOH}\\ \ |\\ \text{H}_2\text{C—COOH}\end{array} + 3\text{CaCl}_2 \longrightarrow \begin{array}{l}\text{HC—COO—Ca—OOC—CH}\\ \ \|\qquad\qquad\qquad\qquad\ \|\\ \text{C—COO—Ca—OOC—C}\\ \ |\qquad\qquad\qquad\qquad\ |\\ \text{H}_2\text{C—COO—Ca—OOC—CH}_2\end{array} + 6\text{HCl}$$

Aconitic acid Tricalcium aconitate

SRRL pioneered initial laboratory studies

To obtain the aconitate necessary for laboratory studies, Godchaux Sugars supplied the Southern Regional Research Laboratory with B molasses, 80° Brix solids, produced at its Raceland mill. This molasses was brought to the laboratory in New Orleans at the close of the 1945 milling season. It contained 3.5 to 3.8% aconitic acid, based on Brix solids. Contrary to experience with molasses from some other mills, no aconitate could be separated from this molasses merely by diluting and heating, nor by heating after adjusting the pH to between 6.5 and 6.8 with lime. Analysis of the molasses revealed that it was low in calcium and magnesium, containing but 0.56 and 0.20%, respectively, based on Brix solids. The molasses did not contain sufficient calcium and magnesium to form insoluble dicalcium magnesium aconitate, and, in addition, a portion of these elements was present in a state unavailable for aconitate formation.

When the molasses was diluted and heated, large quantities of a slimy, amorphous, highly hydrated solid separated, whether lime, calcium chloride, or both, were added to the solution. This material clogged the pores of filter paper or filter cloth almost instantly but could be removed by centrifuging at high speeds. The precipitate, when resuspended in water and centrifuged a second time, was only partially soluble in either strong hydrochloric acid or strong alkali. It could, however, be dried to a hard mass which did not rehydrate to the original slimy condition, and then it could easily be filtered. This washed and dried material contained 11.2% of calcium and 0.8% of magnesium.

Apparently there was competition between the aconitate and the amorphous material for the already insufficient quantity of calcium and magnesium in the molasses. Since the amorphous material was less soluble, and separated first, its precipitation further reduced the amounts of dissolved calcium and magnesium. This work proved that aconitate could be separated only after sufficient calcium had been added to satisfy the requirements of both the amorphous matter and the aconitic acid.

Laboratory tests in which the diluted molasses was limed, treated with calcium chloride, and heated produced a crystalline precipitate, but on cooling these crystals redissolved before they could be separated. When magnesium chloride was also added, the aconitate separated nicely in crystalline form and remained insoluble in the cool molasses.

USDA operated first pilot plant at New Orleans

After these facts had been established in the laboratory, the experiments were transferred to SRRL's pilot plant to ascertain the best procedure for recovering aconitate without impairing the quality of the molasses for further use in sugar manufacture. Runs were made in which the molasses was diluted to Brix solids varying between 45° and 60°. If the dilution was too great, aconitic acid concentration in the resulting solution was low, and the yield of aconitate decreased. When dilution was insufficient, the solution foamed on heating. These results indicated the optimum dilution for the process is 50° to 55° Brix solids. This concentration, fortunately, is satisfactory for returning treated molasses to the sugarhouse for further processing by usual procedures.

The original molasses had a pH of about 5.5, which is too low for maximum precipitation of aconitate. The best agent for adjusting pH is calcium oxide or calcium hydroxide, compared with magnesium oxide, calcined magnesite, potassium hydroxide, and sodium hydroxide. Optimum pH is around 6.5 to 6.8; greater alkalinity causes the solution to foam when heated. If lime is used for the precipitation, it should contain a minimum of carbonate, since the carbon dioxide liberated causes the solution to foam excessively.

Technical grade calcium chloride and magnesium chloride were used to increase the calcium and magnesium content of the solution. A satisfactory addition was found to be 3 parts of anhydrous magnesium chloride for every 5 parts of aconitic acid. Larger quantities of salt have no effect on aconitate recovery; they unnecessarily increase the ash and chloride content of the molasses returned to the sugarhouse. Before chloride addition, the molasses was always diluted, limed, and heated to 120° F. Aconitate began to separate at about 180° F., but the best yields were obtained at temperatures between 200° and 210° F. Temperatures above 210° F. caused excessive foaming and molasses decomposition.

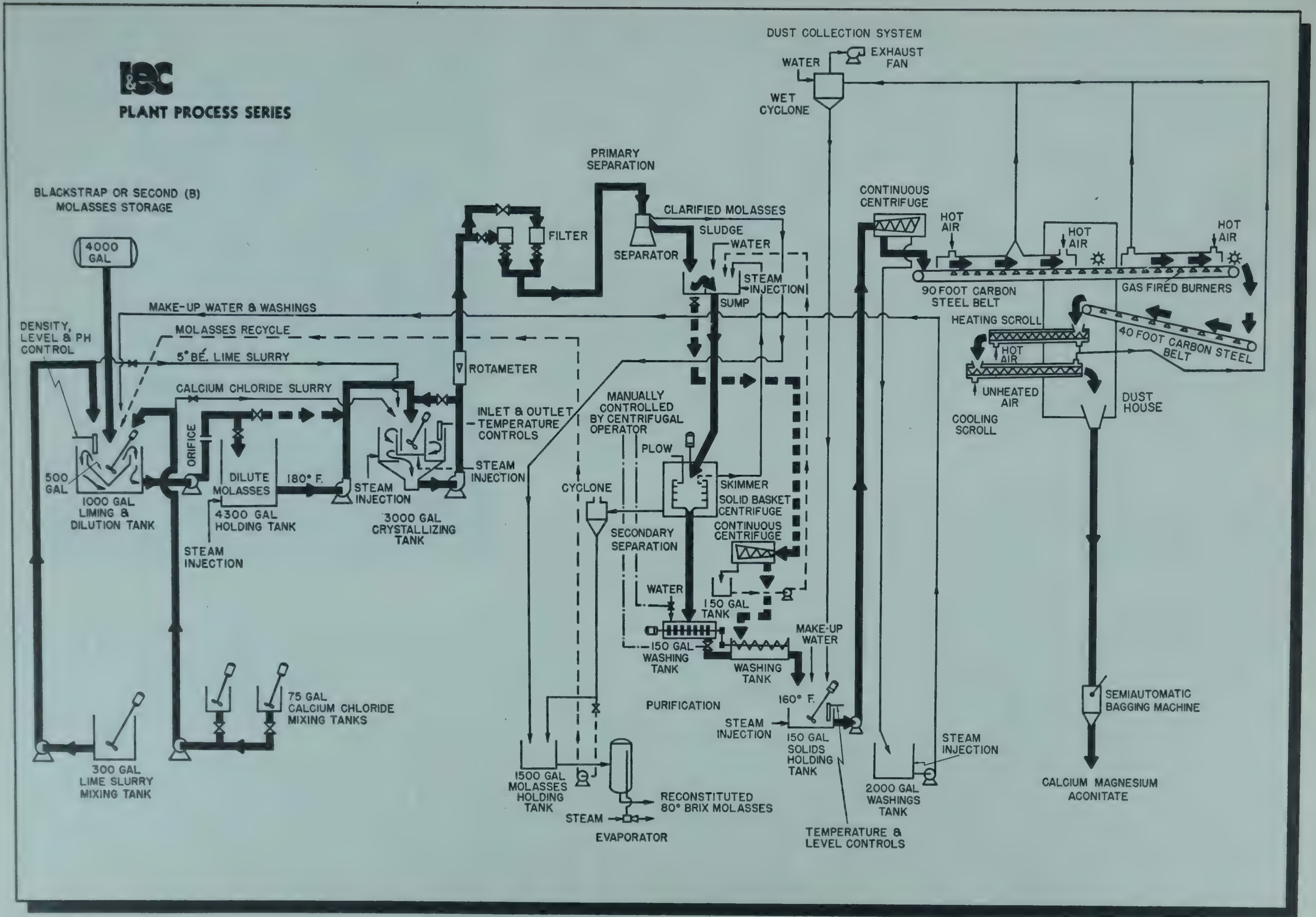

I&EC
PLANT PROCESS SERIES
BLACKSTRAP OR SECOND (B) MOLASSES STORAGE
4000 GAL
MAKE-UP WATER & WASHINGS
MOLASSES RECYCLE
5° BÉ. LIME SLURRY
CALCIUM CHLORIDE SLURRY
DENSITY, LEVEL & PH CONTROL
500 GAL
1000 GAL LIMING & DILUTION TANK
ORIFICE
DILUTE MOLASSES
4300 GAL HOLDING TANK
STEAM INJECTION
180° F.
STEAM INJECTION
3000 GAL CRYSTALLIZING TANK
STEAM INJECTION
INLET & OUTLET TEMPERATURE CONTROLS
ROTAMETER
FILTER
PRIMARY SEPARATION
SEPARATOR
CLARIFIED MOLASSES
SLUDGE
WATER
STEAM INJECTION
SUMP
75 GAL CALCIUM CHLORIDE MIXING TANKS
300 GAL LIME SLURRY MIXING TANK
MANUALLY CONTROLLED BY CENTRIFUGAL OPERATOR
PLOW
CYCLONE
SKIMMER
SOLID BASKET CENTRIFUGE
CONTINUOUS CENTRIFUGE
SECONDARY SEPARATION
WATER
150 GAL TANK
150 GAL WASHING TANK
WASHING TANK
PURIFICATION
1500 GAL MOLASSES HOLDING TANK
STEAM
EVAPORATOR
RECONSTITUTED 80° BRIX MOLASSES
MAKE-UP WATER
160° F.
STEAM INJECTION
150 GAL SOLIDS HOLDING TANK
TEMPERATURE & LEVEL CONTROLS
2000 GAL WASHINGS TANK
STEAM INJECTION
DUST COLLECTION SYSTEM
WATER
EXHAUST FAN
WET CYCLONE
CONTINUOUS CENTRIFUGE
HOT AIR
HOT AIR
HOT AIR
90 FOOT CARBON STEEL BELT
GAS FIRED BURNERS
HEATING SCROLL
HOT AIR
40 FOOT CARBON STEEL BELT
UNHEATED AIR
COOLING SCROLL
DUST HOUSE
SEMIAUTOMATIC BAGGING MACHINE
CALCIUM MAGNESIUM ACONITATE

Figure 1. Flow sheet for production of dicalcium magnesium aconitate from sugar cane molasses at Raceland, La., plant of Godchaux Sugars, Inc.

Investigation showed that during crystallization the temperature must be held at 200° F. for at least 45 minutes; holding the temperature beyond 1 hour has very little effect on aconitate recovery. Aconitate will settle out of solution when the treated molasses is allowed to cool.

It was impossible to filter the aconitate from cool molasses. Large amounts of amorphous, slimy material made separation by settling and decantation unsatisfactory because it prevented the aconitate from sinking and packing. Separation problems were finally solved by centrifuging the whole batch or by partial settling, decanting the supernatant molasses, and centrifuging the bottom slurry. By using a 14-inch solid basket rotating at 1500 r.p.m., the aconitate was thrown out of suspension as a cake while most of the amorphous matter remained in suspension. Aconitate cake was then dropped into hot water, mixed into a slurry, and again passed through the centrifuge at 1500 r.p.m. Water from this operation, containing sugar and very small aconitate crystals, was returned to the process to be used for diluting the molasses and dissolving chemicals for the next batch, thus conserving sugar and supplying seed crystals.

Table I. Distribution Costs of Manufacturing Calcium Magnesium Aconitate

	Manufacturing Cost, %	
	B Molasses	Blackstrap
Chemicals	47.0[a]	21.4
Molasses rental	...	18.9
Labor and supervision	43.6[b]	34.3
Utilities	9.4[c]	25.4

[a] Higher proportion of more expensive calcium chloride, rather than lime, used.

[b] More control analysis labor needed.

[c] Power and steam received from sugar factory during grinding season charged off at lower rate because of higher total power demand.

Godchaux plant processes B molasses and blackstrap molasses

The Godchaux Raceland plant, designed to produce 1,000,000 pounds of aconitate annually, operates continuously for only 7 to 8 months during the year. The unit started up in October 1946 as a pilot plant and semicommercial unit, processing 89° Brix B molasses or 80° to 85° Brix blackstrap molasses. The process flow sheet is shown in Figure 1.

The B molasses comes from the Godchaux sugar factory at Raceland after two strikes of sugar have been removed; reconcentrated molasses leaving the aconitate plant is returned to the sugar factory's pan floor for crystallization of the third sugar strike. Removal of aconitate theoretically improves sugar recovery, because aconitic acid is a melassigenic agent which retards sugar crystallization. The B molasses leaving the aconitate plant is approximately at the normal dilution required for subsequent evaporation to 95° Brix to complete the crystallization of sugar. Therefore, the treating process does not place an appreciable extra heat load on the pans.

Blackstrap molasses (molasses after the third sugar strike is taken) arrives by tank car from nearby mills for processing. This molasses, or equivalent molasses from Godchaux storage, is shipped to its final destination after aconitic acid removal. Molasses free from aconitic acid has improved processing qualities, so Godchaux customers benefit by this "in transit" processing. Treated molasses also has better fermentation properties, but it is not clearly understood whether this is the result of aconitate removal or the removal of other types of nonsugas present in the insoluble material.

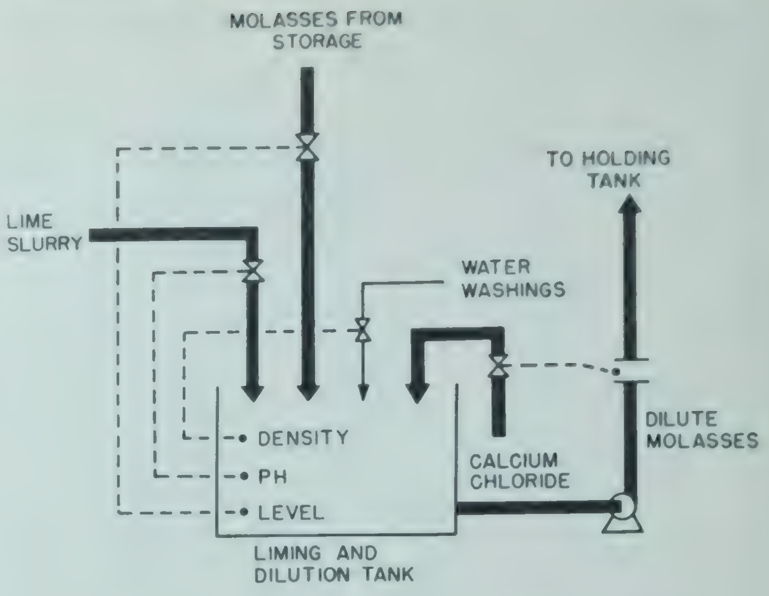
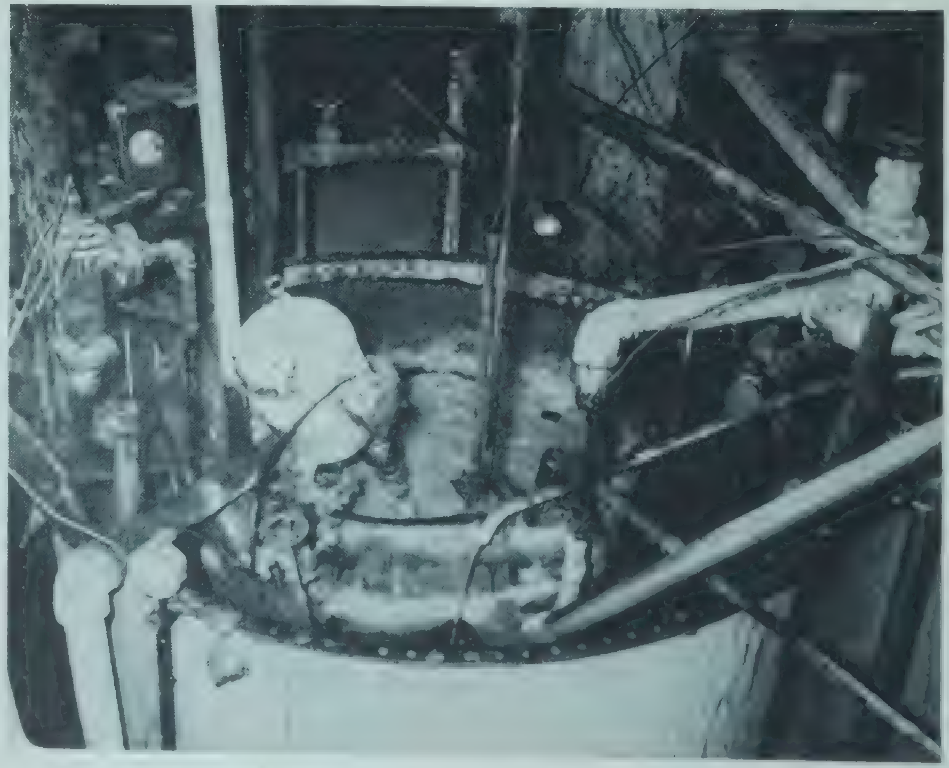


Figure 2. Control system for liming and dilution

While the main product of the Raceland process is dicalcium magnesium aconitate (the lowest solubility salt), the precipitation could theoretically produce tricalcium aconitate, trimagnesium aconitate, or dimagnesium calcium aconitate. There is no evidence, however, of the formation of salts other than dicalcium magnesium aconitate.

Normally it would be expected that both calcium and magnesium chloride would be used to precipitate the mixed salt, but calcium chloride alone is a superior precipitating agent. Raceland molasses and, in general, most Louisiana molasses, contain sufficient magnesium for stoichiometric reaction For economical operation most of the calcium ion is supplied in its cheapest form, as lime, to the final pH adjustment, and the balance is supplied as calcium chloride. If lime were used for complete precipitation, the pH would exceed 7.5, which would destroy the invert sugars. Blackstrap molasses tolerates processing at somewhat higher pH,



First stage in molasses processing—dilution and lining precipitates aconitic acid as dicalcium magnesium salt

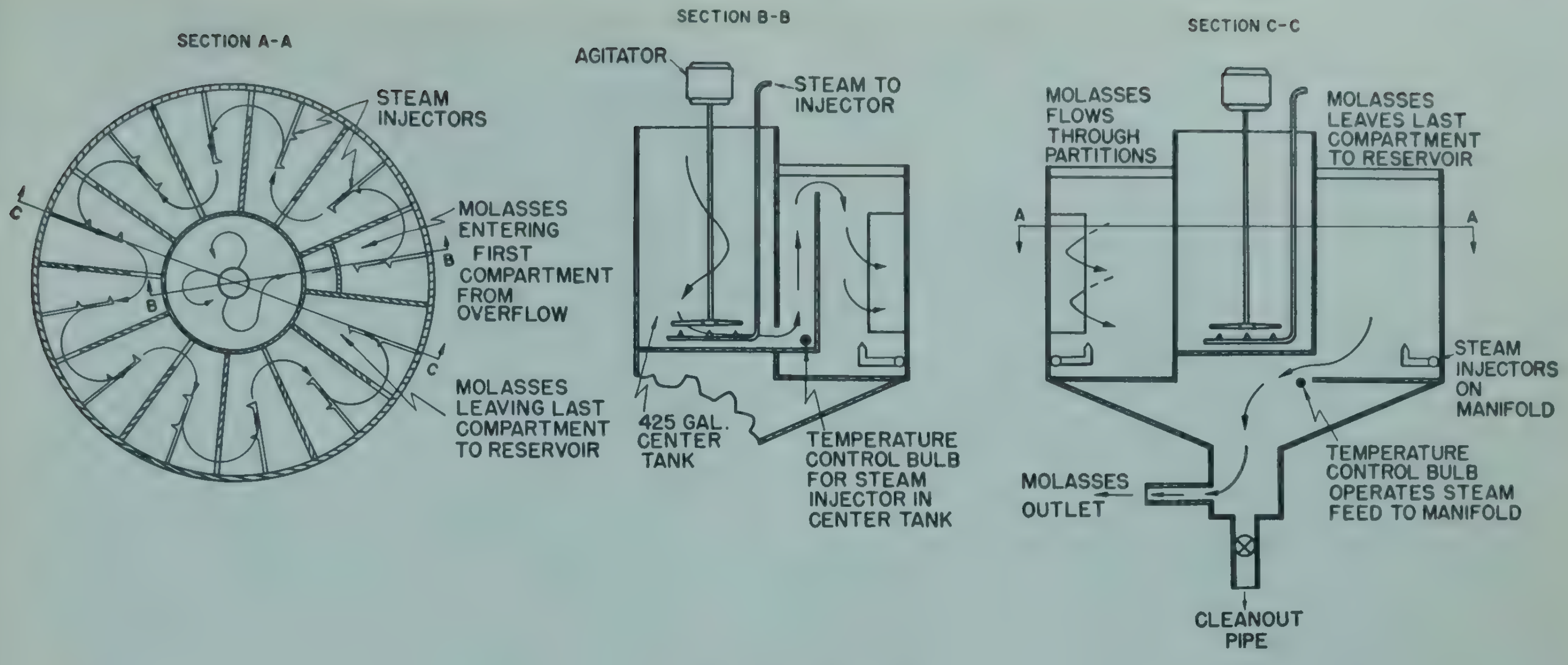

SECTION A-A
STEAM INJECTORS
MOLASSES ENTERING FIRST COMPARTMENT FROM OVERFLOW
MOLASSES LEAVING LAST COMPARTMENT TO RESERVOIR
C
B
B
C
SECTION B-B
AGITATOR
STEAM TO INJECTOR
425 GAL. CENTER TANK
TEMPERATURE CONTROL BULB FOR STEAM INJECTOR IN CENTER TANK
SECTION C-C
MOLASSES FLOWS THROUGH PARTITIONS
MOLASSES LEAVES LAST COMPARTMENT TO RESERVOIR
A
A
STEAM INJECTORS ON MANIFOLD
TEMPERATURE CONTROL BULB OPERATES STEAM FEED TO MANIFOLD
MOLASSES OUTLET
CLEANOUT PIPE

Figure 3. Crystallizer

permitting greater lime to calcium chloride ratios. The effect of this increased lime tolerance is shown by the cost distribution data of Table I.

Aconitate precipitation includes dilution, liming, and crystallization

Molasses, stored in a 4000-gallon tank, is fed to the liming and dilution tank at a rate automatically controlled by the liquid level in the processing vessel (Figure 1). Dilution water, recovered from a later step in the process, is added to bring the Brix of the molasses to approximately 55°. Addition of water is automatically controlled by a specific gravity indicating recorder (Figure 2). Lime slurry (5° Bé.), automatically added to the dilution vessel, raises the solution pH to the desired value, and calcium chloride from a mixing tank completes precipitation of the aconitic acid, in so far as possible. A 15-minute retention time allows essentially complete reaction. Calcium chloride addition is regulated by the flow rate of dilute molasses (through an orifice) leaving the reaction vessel, whereas lime flow is regulated by the solution pH.

Godchaux formerly heated the diluted molasses to about 175° F. with a shell and tube heat exchanger but now uses a steam injected holding tank. The new arrangement eliminates crusting problems encountered in the old exchanger, and the holding tank can be by-passed for periodic cleaning. Coils scale badly in the presence of molasses, so Godchaux uses live steam for all heating purposes in the processing vessels.

In the past, when the sugar factory needed additional storage, it would commandeer the dilute molasses holding tank. Under these conditions, the holding tank was by-passed, so that the liming and dilution tank emptied directly into the crystallizing vessel. Calcium chloride in this case could not be added to the liming and dilution tank, or cold precipitation occurred and clogged the lines, so it was added directly to the center section of the crystallizing vessel.

Dilute molasses from the holding tank remains in the crystallizing tank for 1 hour at 190° F. In earlier operations the residence time was 45 minutes at 200° F., but slightly less than optimum recovery temperature is now used to eliminate foaming and molasses decomposition. Additional lime and calcium chloride are sometimes added to this vessel to maintain the proper pH, because the pH drops when the solution is heated.

Dilute molasses entering the crystallizing vessel (Figure 3) is fed into the center section, which extends slightly above the surrounding baffled compartments. The center section, a 425-gallon tank, is equipped with a motor-driven agitator and a steam injector. A temperature control bulb at the molasses exit regulates the injector.

Total capacity of the entire vessel is 3000 gallons, and the unit is designed for molasses flow in a horizontal direction from wall to wall. Openings between the compartments are nothing more than slots, about 4 by 18 inches. Live steam enters each compartment through injectors connected to a manifold. Each of the 12 equally-sized compartments has its own injectors. A temperature control bulb, located at the molasses exit of the last baffle compartment, operates the steam feed to the manifold. More exact control of each individual compartment is obtained by a valve on its steam injector, in order to maintain all compartments at a uniform temperature.

Molasses flows from the center section of the tank through an overflow and enters the first baffled compartment. It leaves the last baffle compartment (adjacent to the first compartment) through a bottom opening and flows down into a reservoir, the lower part of the crystallizing vessel. This reservoir is equipped with a side molasses outlet and a bottom cleanout pipe. Flow of molasses leaving the crystallizing tank is measured by a rotameter. Flow rate of the entire plant is controlled at this point by an oversize pump and a valved return line to the crystallizing vessel.

Solids separation is key step of process

Molasses from the crystallizing tank enters a disk-type clarifying centrifuge (*4E*) at a flow rate of approximately 2000 gallons per hour. This centrifuge is protected by a twin element line strainer (*3E*) to remove any solids exceeding 0.02 inch. Either filter may be cleaned without interrupting production.

Feed into the centrifuge contains 6 to 10% solids by volume; these solids are 60 to 75% calcium aconitate. Of all the aconitate, both crystalline and in solution, entering the clarifying centrifuge, 65% leaves in the heavy stream and 35% remains in the light stream. Less than 1% of the crystalline aconitate entering is lost to the light stream.

The centrifuge discharges 1700 gallons per hour of clean molasses, from which at least 90%, and sometimes 95%, of the suspended solids have been removed. Solids leaving the separator in the form of a heavy slurry (300 gallons per hour) must then be separated from the residual molasses.

Except for the sludge cover, all parts of the centrifuge in contact with the molasses are stainless steel. The bowl is equipped with six 0.7- or 0.8-mm. carbide nozzles (six blanks). A recirculation assembly, which is optional, may be used to raise the solids concentration of the sludge. Standard purifier-type disks are used with 0.050-inch caulks. The bowl operates at 6200 r.p.m. and is powered by a 20-hp. motor.

This aconitate-loaded sludge enters a sump with baffled compartments. Under normal operating conditions, sludge overflows into the second section for transfer to a solid basket centrifuge (*2E*). A steam injector in the sump keeps the liquid hot, and water can be added to the second section if the sludge is too thick to be handled by the basket centrifuge. This sump contains a measuring device, a 1-gallon pan, to gage the flow from the disk-type centrifuge. Plugging of only one nozzle in the centrifuge is easily detected because of the additional time required to fill the pan. If more than one nozzle is plugged, the equipment is shut down and cleaned. This is almost a 3-hour job for three skilled men working rapidly. To hold shutdown time to a minimum, Godchaux has set up equipment beside the centrifuge to facilitate cleaning, and all workers try to keep the piping system as clean as possible to avoid stoppages.

The basket centrifuge has a baffle bowl of standard design, 40 inches in diameter by 30 inches; the feed rate is such that 15-minute cycles are required to remove solids from the bowl with a hand operated plow. These solids go to a washing tank for purification, while a skimmer removes residual molasses from the basket, for return to the sump. Clarified molasses from the basket centrifuge contains entrapped air, which must be removed by a cyclone separator. If this molasses contains enough aconitic acid, it may be recycled to the liming and dilution tank at the beginning of the process, for additional recovery. Under normal conditions the molasses goes to a holding tank (along with clarified molasses from the disk-type centrifuge), to an evaporator for reconcentration to 80° Brix, and to the sugarhouse for the third strike. (When blackstrap molasses is being treated, this reconcentrated stream goes to storage or tank cars for shipment.)

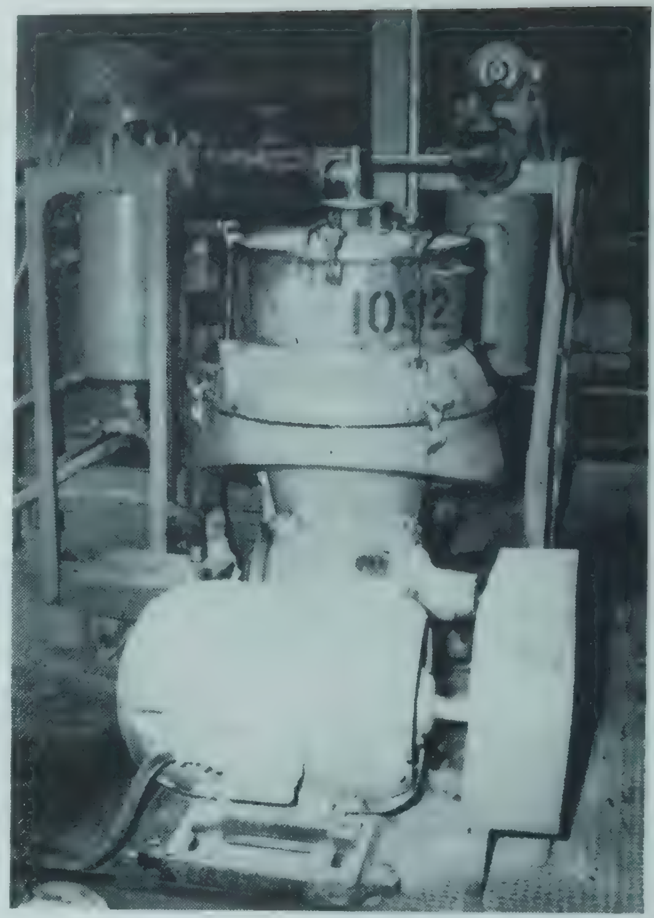
Occasionally, when production exceeds the capacity of the basket centrifuge, a portion of the slurry in the sump is fed to a horizontal centrifuge (*6E*). Solids from this centrifuge pass to the washing scroll immediately following the washing tank in the purification stage. The molasses may still contain considerable solid aconitate, so it is returned to the second compartment of the sump via a holding tank. This procedure is necessary only when a particularly good grade of molasses that produces a high yield of aconitate is treated.

Except for injected steam and the little water that may be added to the sump, most of the water entering the process is wash water added in the purification stage. This is kept to about the quantity required to dilute the incoming molasses. This supply is manually controlled by the basket centrifuge operator. Water may also be added in a solids holding tank immediately following the washing scroll. The temperature in the holding tank is maintained at 160° F. by steam injection, and the liquid level is automatically controlled.

Washed solids are pumped as a slurry to a second horizontal centrifuge (*6E*) for final separation. Solids go to the drying system, and the effluent wash water is returned to the liming and dilution tank via a 2000-gallon holding tank.

Aconitate is dried by gas heated conveyor belts

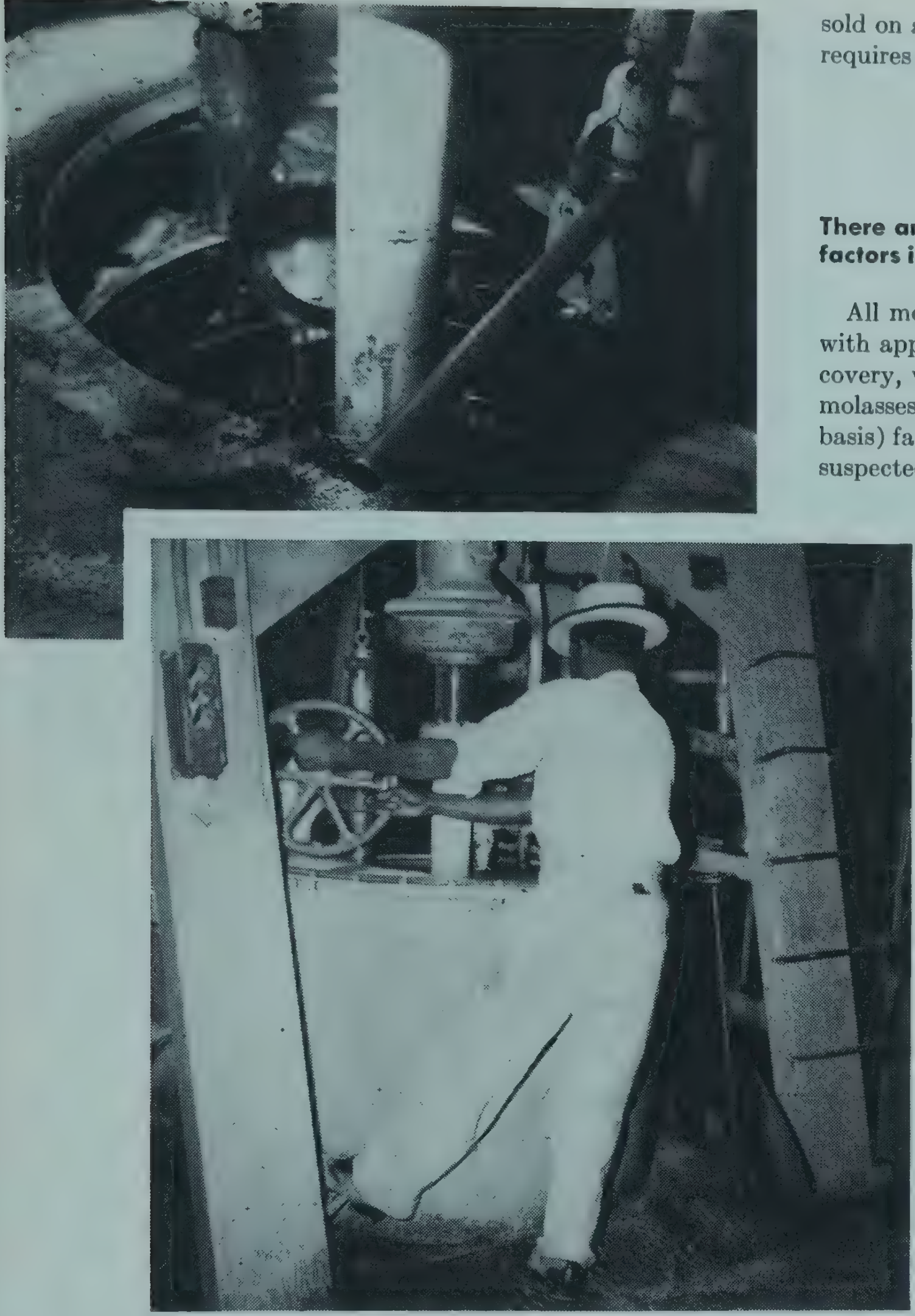
Solids issuing from the second horizontal centrifuge fall onto a slowly moving carbon steel belt which constitutes the first part of the drying system. Aconitate, as it leaves the wash centrifugal, contains approximately 40% moisture and has the consistency and stickiness of peanut butter. The only satisfactory drying equipment found to date is the moving steel belt. As a result of 3 years of development, this drying system evolved from a simple but inadequate design into a rather makeshift but efficient installation. The first belt is direct gas fired, 90 feet long, covered in two sections by a hood. Hot air from a 500,000 B.t.u. atmospheric surface combustion heater enters both sections; dust in the outgoing air passes to a wet cyclone (*1E*) for recovery, and is returned to the solids holding tank immediately following the washing scroll in the purification system. A "kicker" in the center of the belt, between the hoods, is simply a pronged wheel to break up and turn over the solid lumps of aconitate. This belt also has a kicker at the discharge end.



After crystallization, disk-type continuous centrifuge separates 90% of suspended solids

Solids from the first belt fall to a second belt (40 feet long, also heated) and are carried back into the dust house where they drop into an air heated screw conveyor. The 40-foot jacketed conveyor carries aconitate from the dust house and drops it into a second 40-foot screw conveyor cooled by air at room temperature. Cool solids from this conveyor return to the dust house; effluent air from both jacketed conveyors passes to the wet cyclone. Solids leaving the last conveyor fall into a hopper for transfer to the semiautomatic bagging machine (*5E*) and are packed as 100-pound lots in five-ply multiwall paper bags.

Because the Godchaux plant was the first to make calcium aconitate, there was no previous commercial experience with drying the solid to use as a basis for design. The first plant at Godchaux Sugars was to serve as a semicommercial unit, because such a unit cost only slightly more than a smaller pilot plant. The original design called for a 40-foot steel belt and 80 feet of screw conveying equipment for delivery of dry solids to the dust house. Residence time on the belt was to be 30 minutes, and the screw conveyor was to be jacketed and heated with hot air. However, the 40-foot belt was inadequate, and another 90-foot belt was purchased and the system was rearranged to its present form. The long belt has two hoods because Godchaux utilized the original hood designed for the 40-foot belt. It was much easier to run the long belt through the dust house and use the short belt to bring solids back to the dust house than to move the



Solids are removed from residual molasses by basket-type suspended bowl centrifuge

dust house. With adequate belt length, it was no longer necessary to heat both screw conveyors, so the second one now serves to cool the solid product.

Process instrumentation allows efficient use of operating personnel

Plant instrumentation permits a small three-shift operating force of only one plant operator, one centrifuge operator, and one general laborer. The laborer prepares the calcium chloride slurry; he also bags and stores the finished aconitate. Dilute molasses flow rate from the crystallizing tank is adjusted by a single valve; automatic instruments continuously regulate all other liquid and solid flows, pH, density, Brix, and temperature.

One supervisor, working only 8 hours, checks the plant operations in addition to his other duties in the sugar factory. When blackstrap molasses is processed, the operations require one maintenance mechanic during two shifts and one evaporator operator during three shifts. At all other times (during B molasses processing) the evaporator operator and maintenance mechanic are available from the sugar factory. One chemist works one shift at all times. The plant has no sales force since all aconitate is sold on a contract basis. Production of 100 pounds of aconitate requires the following:

Electricity, kw.-hr.	65
Gas, cu. ft.	210
Water, gal.	425
Steam, lb.	3400

There are still unknown factors in aconitate production

All molasses do not react the same way in the process—some with apparently normal aconitic acid content allow very low recovery, while other types give unusually high yields. One type molasses that contained almost 6% aconitic acid (on a dry solids basis) failed to give adequate yields of aconitate. At first it was suspected that there were some discrepancies in the analytical techniques, but the presence of this amount of aconitic acid was confirmed by ion exchange extraction. It is now believed that some other material present in the molasses prevented aconitate precipitation or inhibited crystal growth to such an extent that the small crystals were lost through the centrifuges. Fortunately this situation occurs infrequently. However, it points up the fact that further research on the process is needed to determine all factors involved.

During one grinding season the sugarhouse had considerable difficulty clarifying its cane juice. At this time the operators thought better results might be obtained with hot instead of cold liming. Hot liming of cane juice was tried, and no yield of aconitate was obtained from the resulting molasses, even though analysis indicated its presence. After several days the plant switched to cold liming, and normal aconitate production was resumed. Hot liming was thereafter suspect, until it was tried again and the production was not affected. These experiences further substantiated the theory of the existence of interfering compounds that inhibit precipitation or crystal growth.

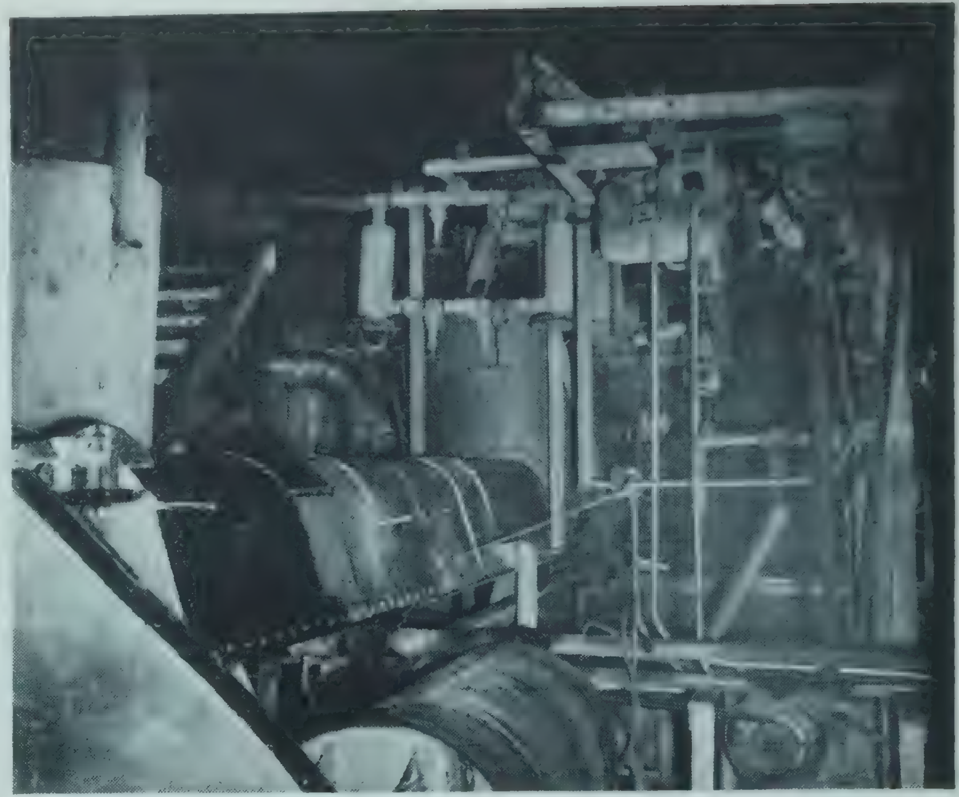
To avoid some of these difficulties, Godchaux has established an extensive system of testing its raw materials. In addition to the possible recovery to be expected, the quantity of calcium chloride and the pH necessary to give optimum yields must be determined. This is accomplished by a double screening program. A sample of molasses collected from the factory is diluted and limed to a standard pH, and a fixed quantity of calcium chloride is added. After the sample is heated to simulated plant conditions, it is placed in a laboratory high speed centrifuge to determine the percentage of solids that separate. If this test indicates suitable recovery, the raw material is accepted. If recoveries are borderline, further tests are conducted with varying calcium chloride addition and pH. A plot of aconitate recovery versus calcium chloride addition indicates whether increased recovery may result from changing these variables. If a suitable set of conditions is found, the molasses is accepted.

During plant operations analyses are made at three points in the process—incoming heavy molasses, outgoing dilute molasses, and the final aconitate product. Small samples of molasses are collected at regular intervals and composited over a 24-hour period, because considerable difficulty has been encountered in developing an automatic sampler. The tendency for such equipment to plug makes continuous sampling impractical.

During the nongrinding season, incoming and outgoing molasses are analyzed for total solids (Brix density), aconitic acid (*1, 2, 22, 23*), and ash content. An aconitic acid balance can be calculated from the aconitic acid–total solids ratio.

Calculated material balances are always compared with actual recoveries.

In addition, during the grinding season, the sugar factory also requires determination of the purity, sucrose content, and glucose (or invert) content of both heavy and dilute molasses. Any sucrose losses (or purity changes) are charged or credited to the aconitate plant. The solid aconitate product is analyzed for total aconitic acid and moisture content during both the grinding and nongrinding seasons; a small sample is collected from each 100-pound bag and composited over a 24-hour period.



Dicalcium magnesium aconitate is purified in washing tank and scroll

Potential raw material supplies are practically unlimited

Production periods are currently limited to 7 or 8 months by availability of suitable raw material. With additional storage, proper scheduling, and swapping of molasses among factories in the area, the operating period could be extended without seriously affecting the process economics. Capacity, of course, can be increased with the present operating period by installation of parallel units.

Leaves of the cane are much higher in aconitic acid content than the stalk, although this source has never been tapped because of the collection and juice extraction problems. Since aconitate recovery developed as a by-product from raw sugar production, cane leaves have been ignored; their juice is low in sucrose and of little value for sugar recovery. Little, if any, research efforts have been concentrated on these problems. In addition, certain cane varieties are much higher in aconitic acid content than those currently processed. These varieties could be cultivated, if the primary interest were aconitate production. High acid cane, however, generally has lower sucrose content and other properties that are objectionable from the sugar recovery standpoint.

Semiautomatic bagging machine packages dried aconitate

Surveys of Louisiana blackstrap molasses have provided a reliable estimate (*11*, *12*, *15*) of the total aconitic acid available from an annual cane crop—about 15,000,000 pounds. By present methods it is feasible to recover one third of this acid, equivalent to almost 10,000,000 pounds of aconitate. Until this potential is realized, little effort will be made to secure new raw material sources.

Ion exchange methods which have been proposed and tried for direct recovery of aconitic acid from molasses depend for economical operation on the ratio of acid anion to the total of all ionic constituents, in terms of chemical equivalents. Cost of regenerants per pound of acid obtained is generally excessive, and the efficiency of separation is impaired if the aconitic anions constitute less than 40% of the total (*12*). Recovery by ion exchange, however, can exceed 90% (more than twice present yields), and molasses of low acid content can be processed, provided the anion ratio is high. Low acid content molasses from western Louisiana factories meet this requirement, including molasses from a few factories in the northern and southern parts of the Louisiana sugar belt. Some of the more modern exchange methods are now being considered as possible process improvements.

The precipitation process itself could probably benefit from the results of more exhaustive research, especially from improved solids separation in the centrifuges. Undoubtedly some fine crystals of aconitate escape through the centrifuges and are discarded with the outgoing molasses. Additives that accelerate crystal growth and result in larger crystals are also under consideration, but most additives are not too effective in viscous solutions. Some molasses appear to be particularly refractory toward crystal growth, probably because of inhibiting agents, and the yield from these molasses is considerably below normal. If this inhibiting effect could be overcome, a greater variety of molasses could be processed.

Elimination of the need for transporting calcium ion from the Raceland plant to the customer who converts calcium magnesium aconitate to the free acid or its esters would result in a considerable freight saving. A logical development would be the establishment of such a converting plant adjacent to the aconitate extraction plant. Inasmuch as Godchaux Sugars is not organized to develop the acid and its esters, nor to market them, such a plant would probably have to be a cooperative venture with an established chemical producer.

Uses of aconitate derivatives may be extended beyond specialty plastics

Outlets for derivatives of aconitic acid have been limited by the current cost of recovery of by-product aconitate. If more efficient recovery methods were devised, higher recoveries would reduce the price of the acid so that larger volumes would be consumed by the chemical industry. Research is continuing on the simple precipitation process for obtaining calcium magnesium aconitate—improvements would require a minimum additional investment in equipment. There is a possibility of increasing the percentage that can be precipitated or devising improvements to permit recovery from certain types of molasses that do not yield the product by the method now used or recovery from substantial quantities of molasses with less than 3% aconitic acid content.

The current price of calcium magnesium aconitate is such that the aconitate esters with desirable plasticizer properties must be sold at prices from 25 to 50% in excess of that of dioctyl phthalate. This premium has restricted the application of aconitates as plasticizers to specialty plastics for which they provide unique properties such as light stability, or demonstrate a substantial margin of superiority. The synthetic detergent field has not been fully explored, but in this application, also, the price of aconitic acid and suitable aconitates is a factor limiting volume consumption.

One possibility for increased recovery at a lower cost is afforded by the application of ion exchange purification to produce direct consumption sugar. Anion exchangers are capable of recovering all of the aconitic acid in molasses of low, as well as high, acid content. Numerous patents on processes for obtaining the acid by ion exchange have appeared, but the proposed methods are uneconomic for the recovery of aconitic acid alone. Recent pilot plant research carried out by the Southern Utilization Research Branch of the United States Department of Agriculture at the Audubon Sugar Factory in Baton Rouge, La., has shown that a noninverting, reverse demineralization procedure can be applied to clarified juice to produce a grade of sugar suitable for direct consumption in candymaking and other industrial sugar uses. Such direct consumption sugar can be produced only during the grinding season, but the increased recovery of sugar per ton of cane may make the process profitable on the basis of sugar production alone. Widespread adoption of this process and development of markets for the grade of sugar produced will make available substantial quantities of anion regenerates containing all the aconitic acid in combination with other impurities removed from the juices so processed. Research will probably be undertaken on economic procedures for isolating and purifying the acid from these regenerates or converting the concentrated crude materials directly to esters or other derivatives suitable for plasticizer and other applications.

Acknowledgment

The authors are indebted to L. F. Martin, E. J. Roberts, and other members of the Sugarcane Products Section, SRRL, for information on laboratory and pilot plant studies conducted by the USDA. Grateful acknowledgment is made for data and helpful suggestions supplied by George C. Conrad of the research department and Benjamin Foret, supervisor of the aconitate plant, Godchaux Sugars, Inc.

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Processing equipment

(1E) American Air Filter Co., Inc., Louisville, Ky., Roto-Clone hydrostatic precipitator, Type **N**.
(2E) Bird Machine Co., South Walpole, Mass., solid basket centrifugal, 40-inch basket.
(3E) Cuno Engineering Corp., Meriden, Conn., Auto-Klean filter, Type **MPM**.
(4E) De Laval Separator Co., Poughkeepsie, N. Y., Nozzle-Matic aconitate separator, special centrifuge, Model **AC-VO** [*De Laval Centrifugal Review* (First quarter, 1949)].
(5E) Exact Weight Scale Co., Columbus, Ohio, Auto-Bagging scale, floor installation unit, Model **2225**.
(6E) Sharples Corp., Philadelphia, Pa., Super-D-Canter centrifugal, Type **P-14**.

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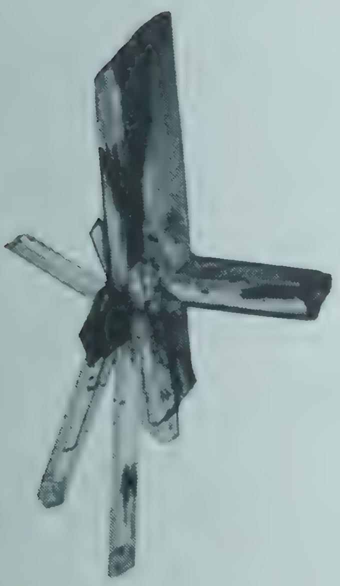

NITROFURANS

HOWARD J. SANDERS, Associate Editor

in collaboration with

ROBERT T. EDMUNDS AND WILLIAM B. STILLMAN

Norwich Pharmacal Co., Norwich, N. Y.

IN 1901 the French chemist, Marquis, reported the first successful direct nitration of furan (*15*). Chemically, the furans are characterized by a five-membered heterocyclic ring consisting of four carbon atoms and one oxygen. Best known of these compounds is 2-furaldehyde (furfural), which contains an aldehyde group in the 2-position—that is, on one of the two carbons nearest the oxygen atom. In the preparation of furan derivatives, the starting material is usually 2-furaldehyde, which, in turn, is produced by the dehydration of five-carbon sugars obtained from corn cobs, oat hulls, and other agricultural wastes (*2*).

Since furan decomposes rapidly in the presence of concentrated acid, early researchers had little success in nitrating this compound. Their work, in progress as far back as 1882, consisted mainly of the nitration of carboxylic acid derivatives of furan and other derivatives stable in acid. Through the efforts of Marquis, a technique was developed of reacting furan directly with a mixture of fuming nitric acid and acetic anhydride. The intermediate was then treated with pyridine to remove the acetate group and form the nitrosubstituted compound.

In the years that followed, research on the nitrofurans was carried out by Gilman and associates at Iowa State College (*9, 10*) and by others. Since 1939, a prime mover in the field has been Norwich Pharmacal Co. Founded in Norwich, N. Y., in 1885, Norwich Pharmacal is well known as a manufacturer of proprietary drugs. Among its most widely used products are such household remedies as Pepto-Bismol, Unguentine, and aspirin.

In search for new antibacterial agents, Norwich entered promising field of nitrofuran chemistry

Wishing to diversify its operations, Norwich in 1939 launched an investigation of antibacterial agents. Originally, the research staff consisted of only two people (the research group today totals more than 65). At the very outset, attention was focused on the furan compounds, for several major reasons. In the first place, furan chemistry was then a relatively unexplored field of pharmaceutical research. At the time, fully 90% of the research on antibacterial agents was concerned with benzene derivatives (*13*). Norwich decided to strike out in a challenging new direction.

As an important consideration, the readily available compound, 2-furaldehyde, held exceptional promise as an inexpensive raw material. Norwich researchers discovered that the addition of a nitro group to the 5-position of the furan ring gave the compound a marked ability either to inhibit the growth of bacteria or to destroy bacteria (*6*). Initial announcement of the bacteriostatic or bactericidal properties of the nitrofurans came in May 1943, when Norwich was issued its first nitrofuran patent (*20*). The company has since received additional patents (*3, 11, 12, 17, 19, 21, 22*) covering various other phases of its nitrofuran research.

Virtually all nitrofurans have been found to possess antibacterial properties. These characteristics are clearly imparted by the nitro group since unnitrated analogs are largely if not totally inactive. The nitrofurans are presumed to operate by inhibiting the enzymatic systems involved in the carbohydrate metabolism of bacteria (*1, 16*).

Table I. Properties of Commercial Nitrofuran Compounds

	Nitrofurazone	Furazolidone	Nitrofurfuryl Methyl Ether	Nitrofurantoin
	5-Nitro-2-furaldehyde semicarbazone	*N*-(5-Nitro-2-furfurylidene)-3-amino-2-oxazolidone	Methyl 5-nitro-2-furfuryl ether	*N*-(5-Nitro-2-furfurylidene)-1-aminohydantoin
Trade name	Furacin	Furoxone	Furaspor	Furadantin
Empirical formula	$C_6H_6N_4O_4$	$C_8H_7N_3O_5$	$C_6H_7NO_4$	$C_8H_6N_4O_5$
Molecular weight	198.14	225.16	157.12	238.16
Color	Pale yellow	Yellow	Pale yellow	Yellow
Melting point, ° C.	236-240° C. (with decomposition)	255	...	270–272° C. (with decomposition)
Boiling point, ° C.	...	...	104–105 at 3 mm. Hg	...
Refractive index	...	...	1.5355 at 20° C.	...
Crystal form	Needles in two polymorphic forms	...	...	Prismatic needles
Stability	Sensitive to alkaline soln.	86% after 24 hr. at 25° C., in water	...	99% after 24 hr. at 37° C., in water
Acid constant, pK_a	10.0	...	...	7.2
Solubility, mg./liter				
Water	210	40	11,000	190 (at pH 7)
95% ethyl alcohol	920	90	Infinite	510
Acetone	1830	...	...	5100
Dimethylformamide	67,000	10,000	...	80,000
Peanut oil	15	10	170,000	20.7
Glycerol	935	...	...	600
Polyethylene glycol 300	11,700	1320	...	15,000

The first testing of nitrofurans on humans took place at a military hospital in England in June 1944. Crowded with soldiers wounded during the invasion of Normandy, the hospital found itself faced with dozens of cases of burns and wounds that had become dangerously infected and refused to heal. Conventional methods of treatment were less than satisfactory. Fortunately, one doctor on duty, M. L. Snyder, had recently learned of research in the U. S. on the nitrofurans. Would these new antibacterial agents work on humans? Norwich quickly forwarded trial quantities of several of its most promising nitrofuran compounds.

Results far exceeded expectations. Especially encouraging was the effectiveness of nitrofurazone (5-nitro-2-furaldehyde semicarbazone). Tests on numerous bacterial cultures from war wounds and burns showed that, although heavy bacterial growth occurred in 63% of the cultures before nitrofurazone treatment, there was comparable growth in only 4% of the cases after treatment (*18*). In a matter of months, the drug was being tested at Rhoads Military Hospital in Utica, N. Y., the University of Maryland, Boston City Hospital, and elsewhere.

In tests on a new nitrofuran, oral dose is given to a laboratory mouse

In 1946, Norwich established a separate division, Eaton Laboratories, to carry forward its investigations of the nitrofurans. As an outgrowth of this research, four nitrofurans have reached commercial status—nitrofurazone (Furacin), introduced commercially in 1944, nitrofurfuryl methyl ether (Furaspor) in 1948, furazolidone (Furoxone) in 1952, and nitrofurantoin (Furadantin) in 1953. The physical properties of these compounds are indicated in Table I.

Today, Norwich is the sole producer, on a commercial scale, of nitrofuran compounds in the United States. Various companies in Britain, France, Italy, Germany, Sweden, and The Netherlands are marketing these drugs under license from Norwich. In recent years, so widespread has been the interest in these compounds that technical reports on the nitrofurans can be found in more than 900 scientific publications in 17 languages. Thus far, Norwich has synthesized and tested over 300 different nitrofurans. In addition, it has investigated about 200 other derivatives of furan.

Uses for nitrofurans extend into fields of both human and veterinary medicine

The nitrofurans find important application in human as well as veterinary medicine. In human therapy, they are used both topically, as in the case of nitrofurazone, and orally, in the case of nitrofurantoin.

The first nitrofuran developed commercially, nitrofurazone, is today by far the most widely used. In human medicine, its major application is in the prevention and treatment of surface infections in wounds, burns, skin grafts, and surgery (*14*). The drug also finds use in the treatment of eye, ear, and nose disorders and as an ingredient in urethral and vaginal suppositories (*7*).

In 1947, Paul D. Harwood of Dr. Hess & Clark, Inc., found that nitrofurazone is effective in preventing coccidiosis in chickens and enteritis in swine. Since 1950, Dr. Hess & Clark has been marketing a feed supplement containing Norwich's nitrofurazone for animal disease control. This use is by far the largest single market for nitrofurazone. The drug is also widely employed in the treatment of mastitis in cows, in which case it is sometimes used in combination with an antibiotic such as penicillin.

The second nitrofuran introduced commercially, nitrofurfuryl methyl ether (methyl 5-nitro-2-furfuryl ether), is the only one currently available for the treatment of fungus infections. It is used mainly as a topical application in the treatment of ringworm in humans and ear infections and skin disorders in animals.

Second to nitrofurazone, the nitrofuran most widely used in

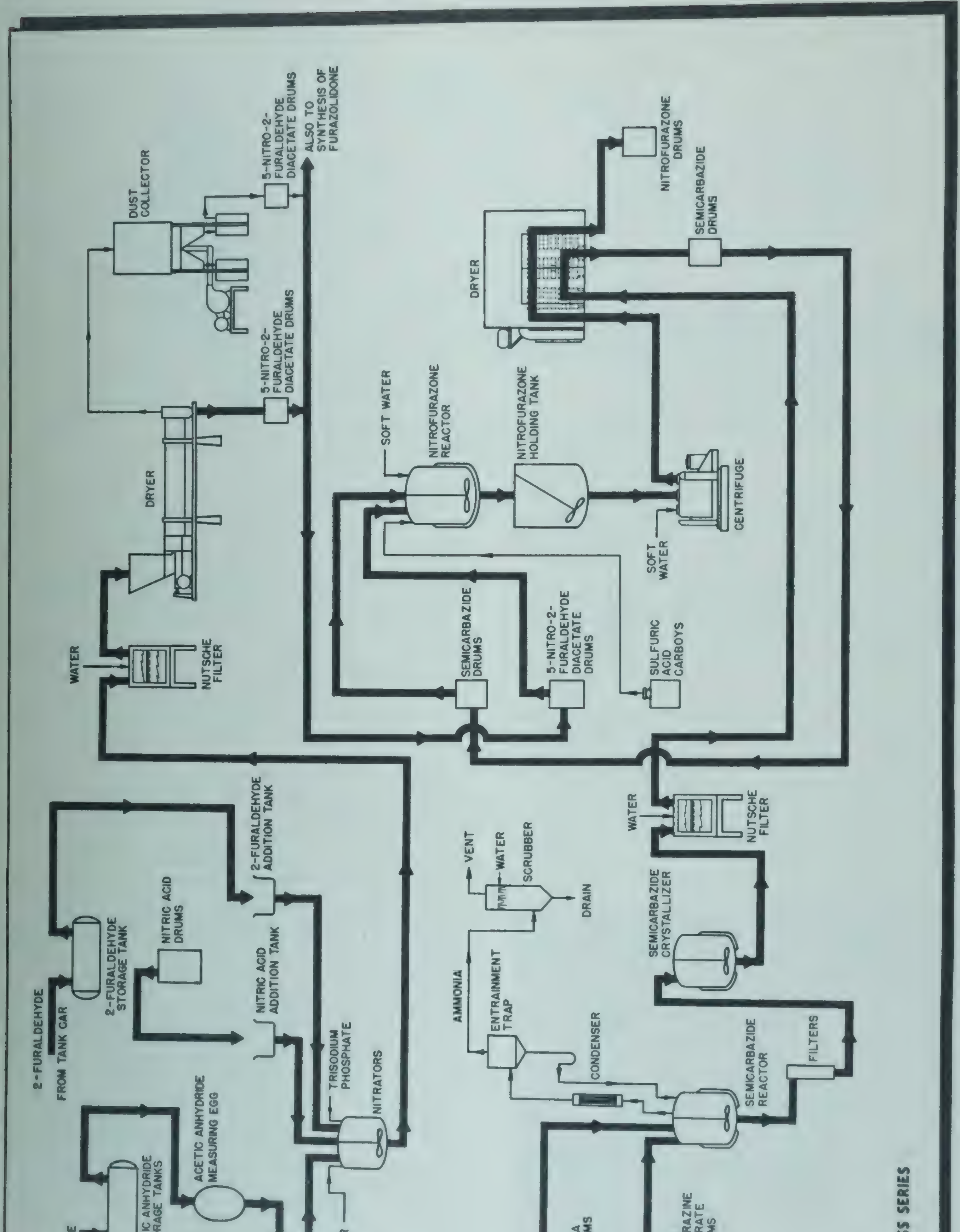
ACETIC ANHYDRIDE
FROM TANK CAR
ACETIC ANHYDRIDE STORAGE TANKS
ACETIC ANHYDRIDE MEASURING EGG
STRAINER
WATER
2-FURALDEHYDE
FROM TANK CAR
2-FURALDEHYDE STORAGE TANK
NITRIC ACID DRUMS
NITRIC ACID ADDITION TANK
2-FURALDEHYDE ADDITION TANK
TRISODIUM PHOSPHATE
NITRATORS
WATER
NUTSCHE FILTER
DRYER
5-NITRO-2-FURALDEHYDE DIACETATE DRUMS
DUST COLLECTOR
5-NITRO-2-FURALDEHYDE DIACETATE DRUMS
5-NITRO-2-FURALDEHYDE DIACETATE DRUMS
ALSO TO SYNTHESIS OF FURAZOLIDONE
SOFT WATER
NITROFURAZONE REACTOR
NITROFURAZONE HOLDING TANK
SEMICARBAZIDE DRUMS
5-NITRO-2-FURALDEHYDE DIACETATE DRUMS
SULFURIC ACID CARBOYS
SOFT WATER
CENTRIFUGE
DRYER
SEMICARBAZIDE DRUMS
NITROFURAZONE DRUMS
VENT
WATER
SCRUBBER
DRAIN
AMMONIA
ENTRAINMENT TRAP
CONDENSER
WATER
NUTSCHE FILTER
SEMICARBAZIDE CRYSTALLIZER
FILTERS
SEMICARBAZIDE REACTOR
UREA DRUMS
85% HYDRAZINE HYDRATE DRUMS
I&EC
PLANT PROCESS SERIES

Figure 1. Flow sheet for production of nitrofurazone, Norwich Pharmacal Co., Norwich, N. Y.

the veterinary field is furazolidone [*N*-(5-nitro-2-furfurylidene)-3-amino-2-oxazolidone]. This drug, not yet employed in human therapy, finds important application in the control of chicken and turkey diseases.

Newest of the nitrofurans for use in human medicine is nitrofurantoin [*N*-(5-nitro-2-furfurylidene)-1-aminohydantoin], which is employed increasingly in the treatment of urinary tract infections (*4*, *5*, *8*). Even though therapeutic dosages of nitrofurantoin do not produce detectable concentrations in the blood, highly effective antibacterial concentrations in the urine are attained within 30 minutes.

In many of their applications, the nitrofurans are in direct competition with such other antibacterial agents as the sulfa drugs and the antibiotics. One of the special merits of the nitrofurans is their ability to act effectively against a broad range of microorganisms. At the same time, they produce few undesirable side effects. With the nitrofurans, the development of bacterial resistance is negligible, and the drugs can be used in extremely low concentration. In addition, they are often less costly than other drugs designed for the same purpose.

Norwich produces nitrofurazone and furazolidone in commercial scale facilities located about 3 miles from the company headquarters in downtown Norwich The nitrofurazone plant, which is adjacent to the aspirin plant, was completed in December 1951. Previously, the drug had been manufactured in pilot plant equipment at the downtown plant. The present large scale facilities, occupying an area of 60 × 80 feet, have the capacity to produce about 250,000 pounds of nitrofurazone a year. The furazolidone plant, which is an extension of the nitrofurazone installation, was completed in April 1954. Capable of producing 50,000 pounds of furazolidone a year, this plant consists of one room, 40 × 40 feet, for processing and another room of equal size for drying and milling.

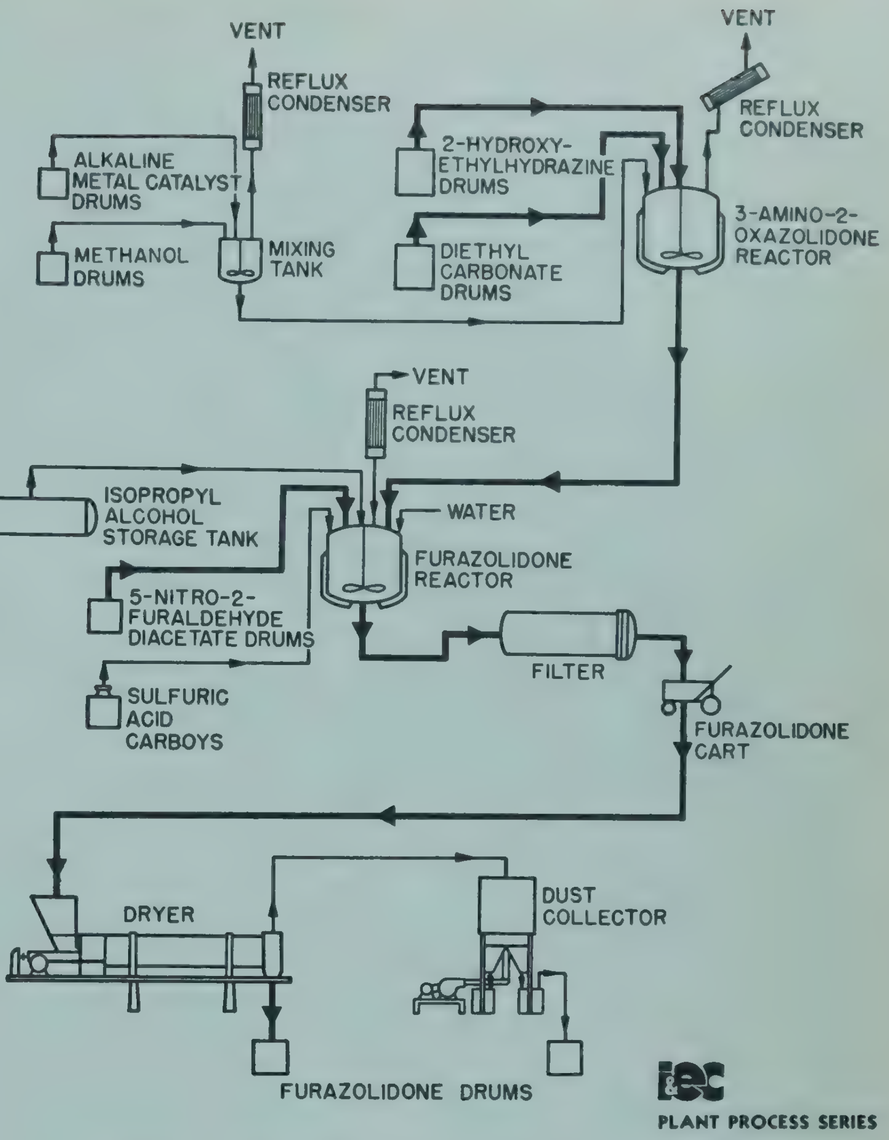
VENT
REFLUX CONDENSER
ALKALINE METAL CATALYST DRUMS
METHANOL DRUMS
MIXING TANK
VENT
2-HYDROXY-ETHYLHYDRAZINE DRUMS
DIETHYL CARBONATE DRUMS
REFLUX CONDENSER
3-AMINO-2-OXAZOLIDONE REACTOR
VENT
REFLUX CONDENSER
ISOPROPYL ALCOHOL STORAGE TANK
WATER
FURAZOLIDONE REACTOR
5-NITRO-2-FURALDEHYDE DIACETATE DRUMS
SULFURIC ACID CARBOYS
FILTER
FURAZOLIDONE CART
DRYER
DUST COLLECTOR
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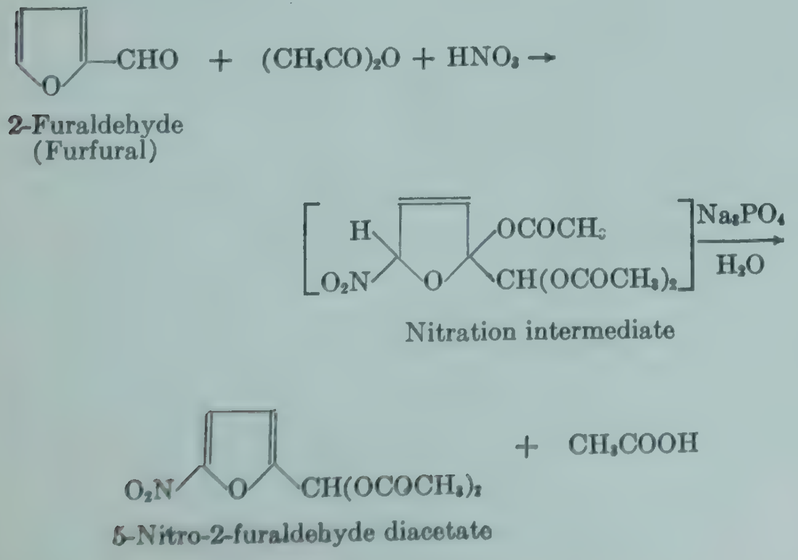
Figure 2. Flow sheet for production of furazolidone

Synthesis of 5-nitro-2-furaldehyde diacetate is initial phase of batchwise procedure

The first phase of the production of both nitrofurazone and furazolidone (outlined in the flow sheets of Figures 1 and 2) is the preparation of 5-nitro-2-furaldehyde diacetate:


CHO
$(CH_3CO)_2O + HNO_3$
H
O_2N
O
$OCOCH_3$
$CH(OCOCH_3)_2$
Na_3PO_4
H_2O
O_2N
O
$CH(OCOCH_3)_2$
$+ CH_3COOH$

2-Furaldehyde (Furfural)

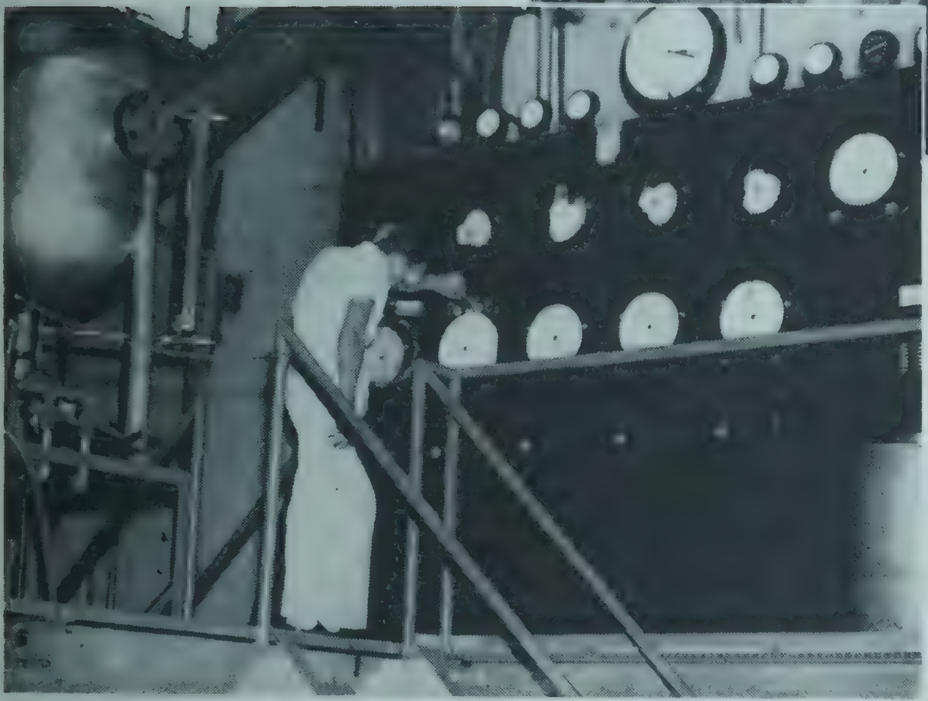
Nitration intermediate

5-Nitro-2-furaldehyde diacetate

The first step consists of the formation of a nitration intermediate by the addition of 2-furaldehyde (furfural) to a nitrating mixture composed of acetic anhydride and concentrated nitric acid. In the plant (Figure 1), the acetic anhydride is discharged by 15-pound-per-square-inch compressed air from a tank car into one of two 16,000-gallon aluminum storage tanks. It is transferred by vacuum into a 200-gallon aluminum measuring egg (*2E*). The desired amount of acetic anhydride, measured by a liquid level indicator, passes through a strainer that removes any solid contaminants. The anhydride then flows by gravity into any one of five identical nitrators (*2E*). Five nitrators, rather than a single unit, are used to permit effective cooling by the internal cooling coils. In the nitration step, approximately 60,000 B.t.u. are liberated for every 30 gallons of reaction mixture. The nitrators are 100-gallon aluminum units equipped with stainless steel agitators and stainless steel coils for heating or cooling. Although stainless steel is the preferred material of construction for the nitrators, aluminum was selected because of the difficulty of obtaining stainless steel during the Korean War.

After the acetic anhydride is charged, 70% nitric acid from 55-gallon drums is pumped into an 8-gallon stainless steel addition tank. The required amount of nitric acid, measured by a liquid level indicator, gradually flows into the nitrator under continuous agitation. During the exothermic reaction of acid and anhydride, the temperature is automatically controlled at about 25° C. Should the temperature rise above this level, the rate of acid addition is automatically reduced and the rate at which the 2° C. cooling water is circulated through the coils is automatically in-

Nitrators used in synthesis of 5-nitro-2-furaldehyde diacetate are at left; reactors used in preparation of nitrofurazone are at right



On panel board are mounted instruments for control of nitration step in synthesis of 5-nitro-2-furaldehyde diacetate

creased. Although the reaction temperature is not critical, wide temperature fluctuations are avoided.

The 2-furaldehyde, delivered by tank car, is stored in a 10,000-gallon underground iron tank. The material is pumped into an 8-gallon aluminum addition tank; the desired amount is measured by a liquid level indicator. After the required amount of nitric acid is charged to the nitrator, the 2-furaldehyde is added. The addition rate and cooling water rate are automatically controlled to maintain the reaction temperature at about 25° C. During this addition, which is carried out in an excess of acetic anhydride, the 2-furaldehyde reacts with the acetic anhydride to form 2-furaldehyde diacetate. The diacetate is then nitrated to form the so-called nitration intermediate.

After the addition of 2-furaldehyde, the reactants are agitated for an additional half hour at a temperature of 40° C., controlled automatically with steam-heated tap water in the coils. Immediately after the reaction is completed, the nitrator is almost completely filled with tap water to cool and quench the reaction mixture.

Base is added to raise the pH to about 3.7. Trisodium phosphate, obtained in 100-pound bags, is used for this purpose because of its ease of handling. The phosphate-buffered reaction mixture is held at about 55° C. for 1 hour and then automatically cooled to about 25° C. by pumping tap water through the coils. The 5-nitro-2-furaldehyde diacetate gradually crystallizes in the form of sugarlike particles that are readily suspended.

The slurry is fed onto a 4-foot-diameter wooden nutsche filter (*11E*) covered with a 35 × 250 mesh stainless steel wire cloth. Two filters are used for this purpose, each capable of handling three or four nitration batches. The filtrate goes to the waste treatment plant for the recovery of 99.0% acetic acid, which is sold.

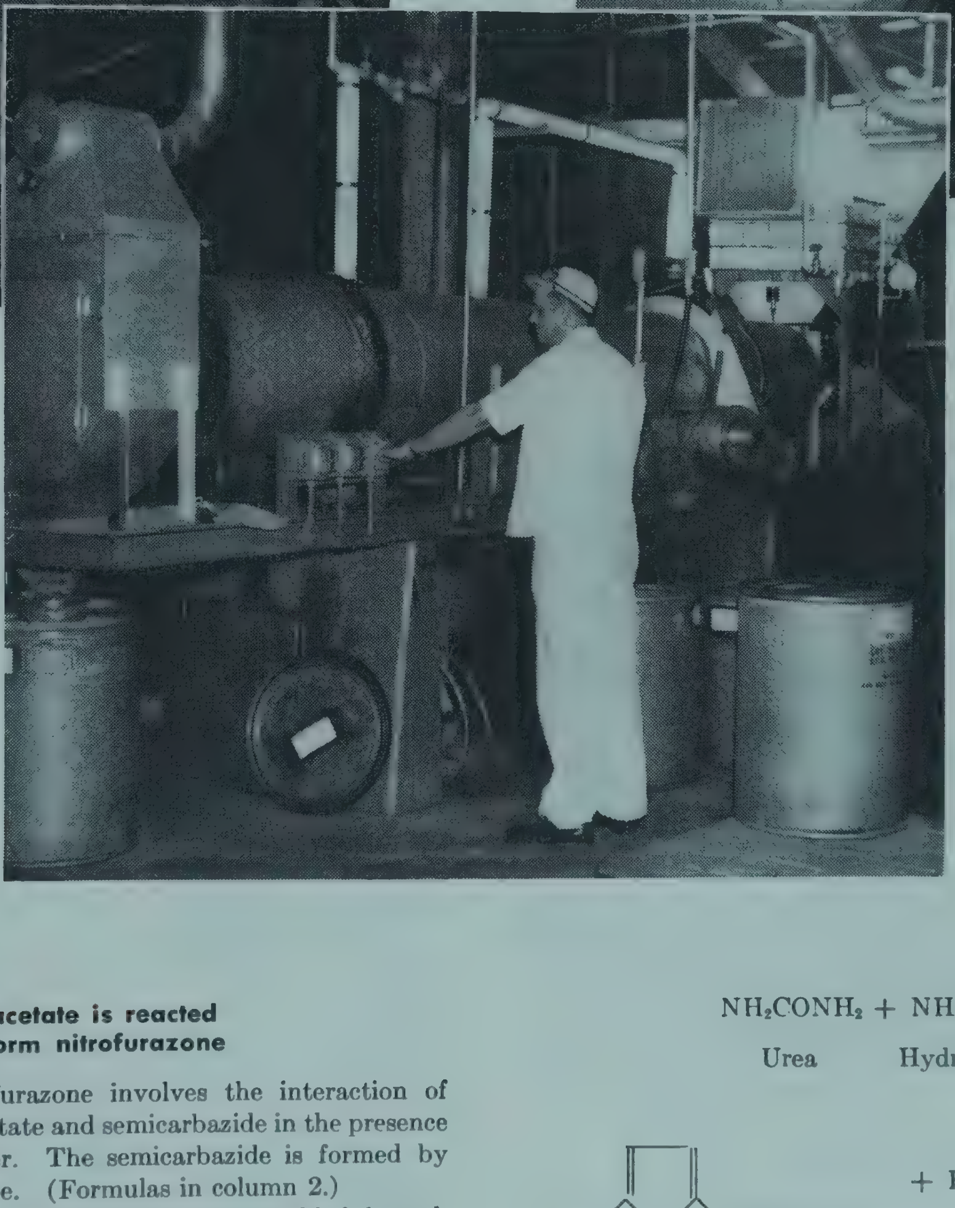
The filter cake is water-washed to remove the excess acetic acid. The cake is then transferred to the nearby hopper of a rotary hot-air drum dryer (*6E*). This dryer, 15 feet long and 2 feet in diameter, contains a series of flights which, as the drum slowly rotates, continuously mixes the material and moves it toward the exit. At the same time, a blower draws a steady, concurrent stream of heated air through the dryer and out through the dust collector (*3E*).

Most of the dried 5-nitro-2-furaldehyde diacetate is collected in drums at the exit of the dryer. The remainder is recovered at the base of the dust collector, which contains several cloth bags that force the escaping air to deposit its entrained solid particles. Countercurrent air jets that move up and down the length of the bags prevent the cloth from becoming plugged by solids. The drying operation is completed in about 25 minutes.

The dried 5-nitro-2-furaldehyde diacetate then goes directly into the preparation of technical grade nitrofurazone or furazolidone. When the diacetate is used in the preparation of drugs for human use, such as NNR (new and nonofficial remedies) nitrofurazone and nitrofurantoin, it is first purified. Purification consists of dissolving the 5-nitro-2-furaldehyde diacetate in isopropyl alcohol at 73° C., filtering in the presence of activated charcoal, cooling to 20° C., recrystallizing, filtering, and drying.

▲ Line filter is used when recrystallization of 5-nitro-2-furaldehyde diacetate is required; recrystallization tanks are in background

▲ Filtered diacetate is transferred from suction nutsche to hopper of rotary drum dryer



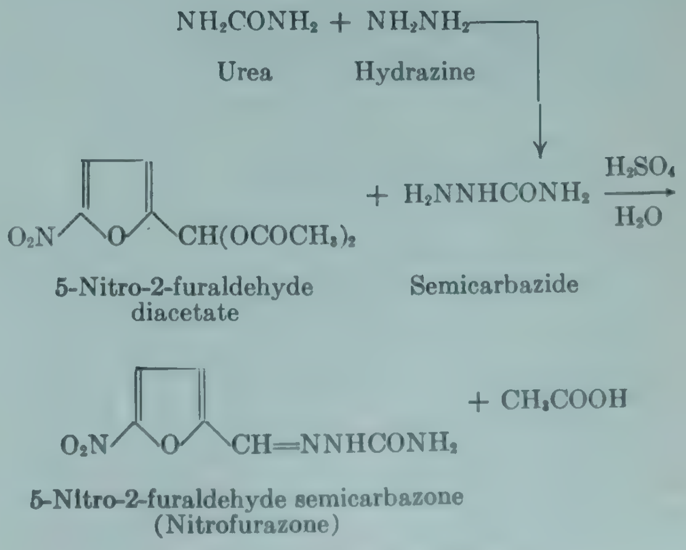
◀ 5 - Nitro - 2 - furaldehyde diacetate is dried in 15-foot-long hot air rotary dryer

5-Nitro-2-furaldehyde diacetate is reacted with semicarbazide to form nitrofurazone

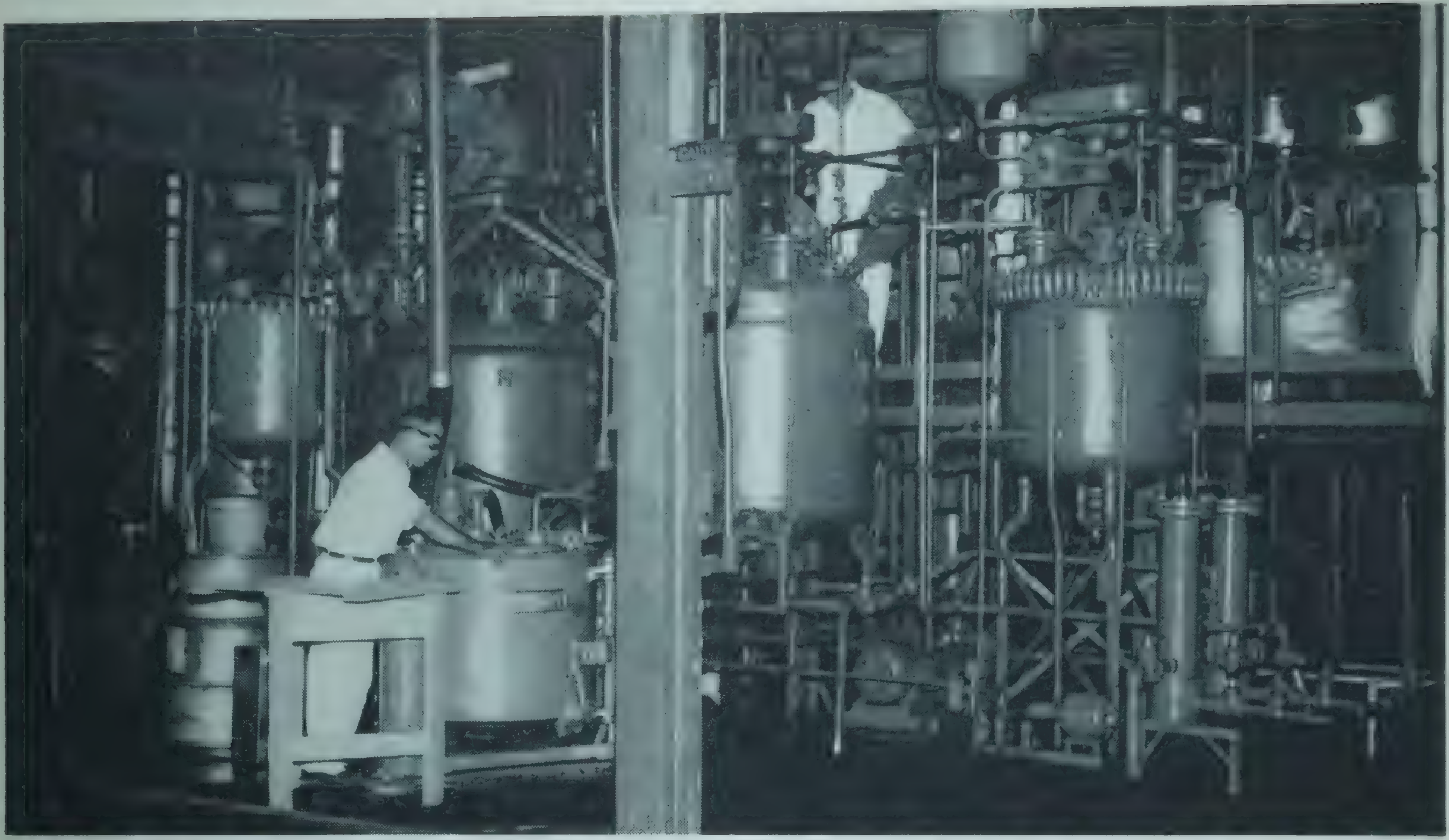
The synthesis of nitrofurazone involves the interaction of 5-nitro-2-furaldehyde diacetate and semicarbazide in the presence of sulfuric acid and water. The semicarbazide is formed by reacting urea and hydrazine. (Formulas in column 2.)

First, the urea, obtained in 200-pound drums, is added through the hatch of the semicarbazide reactor (*8E*), which is a 100-gallon stainless steel, jacketed, agitated kettle. Hydrazine, in the form of 85% hydrazine hydrate, is charged from a 55-gallon drum. Both the hydrazine hydrate drum and the pipe leading to the reactor are grounded to prevent the possibility of static electricity igniting the hydrazine.

The reactants are heated at about 100° C. for 5 hours. A by-product of the reaction is ammonia, which passes up through a 6-foot-long stainless steel condenser that cools the gas from 100° to 60° C. The ammonia, which also contains entrained hydrazine and water, goes to a stainless steel centrifugal trap,


NH_2CONH_2 + NH_2NH_2
Urea
Hydrazine
O_2N
O
$CH(OCOCH_3)_2$
+ $H_2NNHCONH_2$
H_2SO_4
H_2O
5-Nitro-2-furaldehyde diacetate
Semicarbazide
O_2N
O
$CH{=}NNHCONH_2$
+ CH_3COOH
5-Nitro-2-furaldehyde semicarbazone (Nitrofurazone)

Preparation of Nitrofurazone



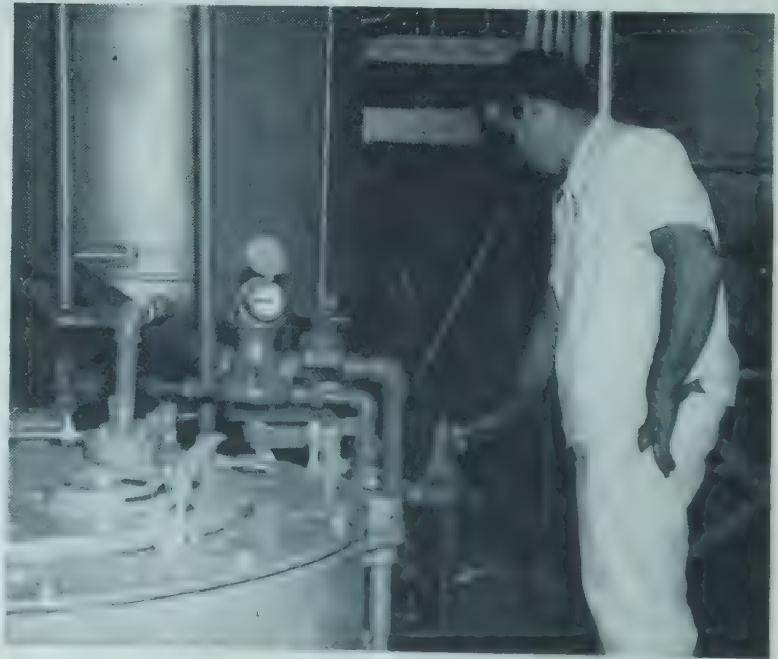
Main processing section of nitrofurazone plant. From left to right are receiving tank, nitrofurazone reactor, 30-inch centrifuge, and semicarbazide crystallizer and reactor

Semicarbazide is transferred from dryer tray to drums, stored briefly, and then used in preparation of nitrofurazone

where the entrained material is collected and later returned to the reactor. The gas leaving the trap passes into a water scrubber—an iron tower, 8 feet high and 1.5 feet in diameter, equipped with spray nozzles. The water, which picks up virtually all of the ammonia by solution, is discarded, while the exit gas is discharged to the atmosphere.

Once the reaction of urea and hydrazine is complete, the reactor is cooled to about 35° C. by circulating tap water in the jacket. The contents of the reactor are then sent through either one of two porous stone filters (*1E*) that remove small quantities of such insoluble by-products as biuret and hydrazodicarbonamide. The filtered solution is pumped into a 200-gallon stainless steel, jacketed, agitated crystallizer (*8E*), where it is cooled to 15° C. by well water in the jacket. After the semicarbazide has crystallized, it is pumped to a 4-foot-diameter wooden nutsche filter (*11E*) covered with 35 × 250 mesh stainless steel wire cloth. It is then sent to a batch tray dryer, where it is dried at 60° C. for 16 hours.

In the next step, the 300-gallon, glass-lined, jacketed, agitated nitrofurazone reactor (*8E*) is charged with treated water. This water is free of metallic ions, thus eliminating the possibility that a metallic salt will later precipitate and contaminate the final



Slurry is fed from holding tank to rubber-covered centrifuge; nitrofurazone is then dried in batch tray dryer product. A glass-lined kettle is used to prevent color contamination. To the reactor is also added 94% sulfuric acid from 12-gallon carboys. The 5-nitro-2-furaldehyde diacetate and the semicarbazide are charged. These materials are heated at about 90° C. for 2 hours. During this period, the nitrofurazone is formed and begins to precipitate. The yield in this step approaches theoretical.

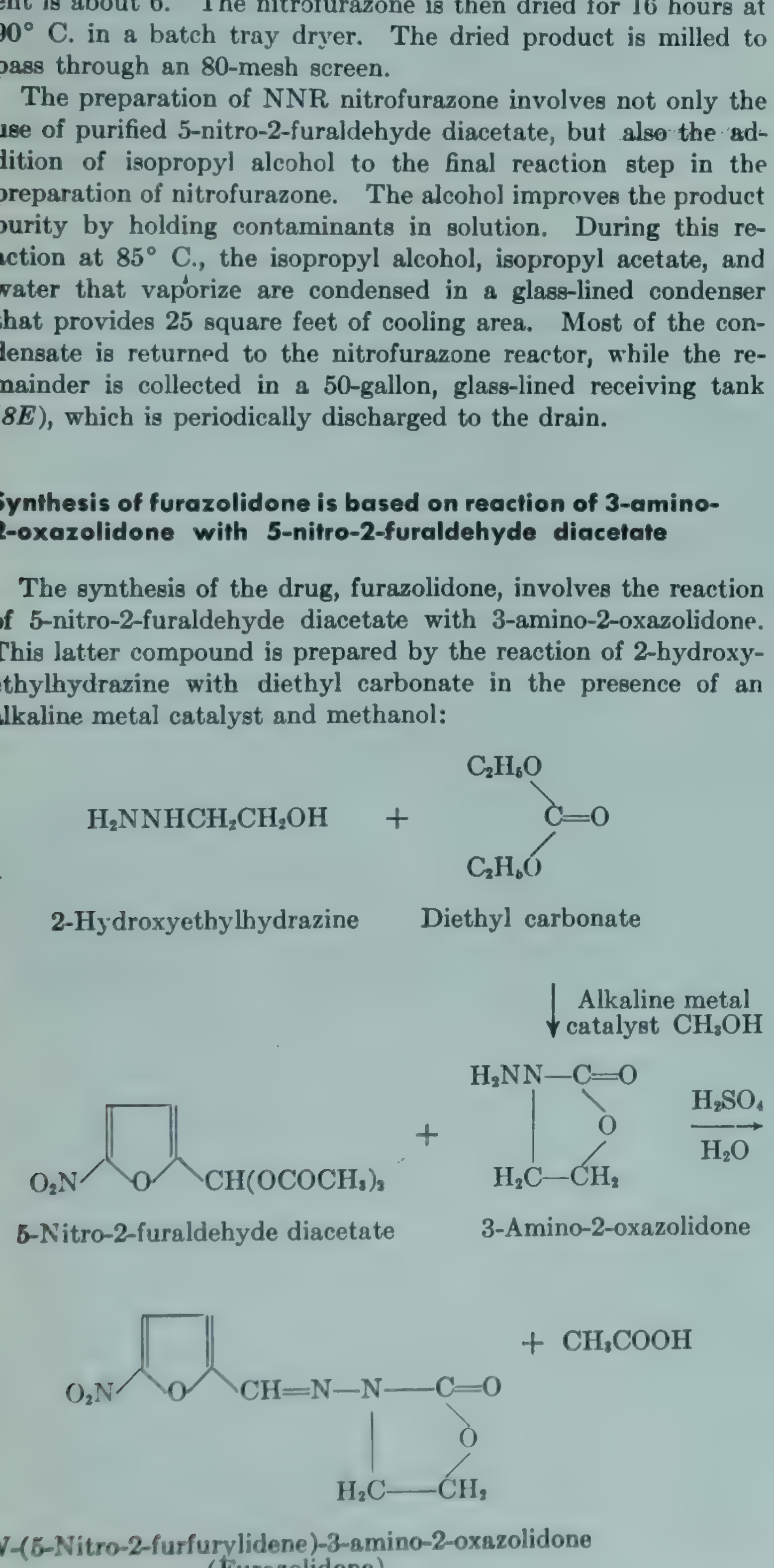
The slurry is cooled to 20° C. and pumped into a 300-gallon, glass-lined, agitated holding tank (*8E*). This unit permits the nitrofurazone reactor to be used promptly for the next batch, which might otherwise be delayed during the subsequent, relatively slow centrifugation step.

The slurry is pumped from the holding tank into a 30-inch-diameter, rubber-covered, center-slung centrifuge (*4E*) which employs a cloth bag as the filtering medium. The centrifuge can handle about one third of a batch per cycle. After centrifugation, the product is washed with treated water to remove the acetic acid previously formed during the reaction, as well as the sulfuric acid. Washing is continued until the pH of the effluent is about 6. The nitrofurazone is then dried for 16 hours at 90° C. in a batch tray dryer. The dried product is milled to pass through an 80-mesh screen.

The preparation of NNR nitrofurazone involves not only the use of purified 5-nitro-2-furaldehyde diacetate, but also the addition of isopropyl alcohol to the final reaction step in the preparation of nitrofurazone. The alcohol improves the product purity by holding contaminants in solution. During this reaction at 85° C., the isopropyl alcohol, isopropyl acetate, and water that vaporize are condensed in a glass-lined condenser that provides 25 square feet of cooling area. Most of the condensate is returned to the nitrofurazone reactor, while the remainder is collected in a 50-gallon, glass-lined receiving tank (*8E*), which is periodically discharged to the drain.

Synthesis of furazolidone is based on reaction of 3-amino-2-oxazolidone with 5-nitro-2-furaldehyde diacetate

The synthesis of the drug, furazolidone, involves the reaction of 5-nitro-2-furaldehyde diacetate with 3-amino-2-oxazolidone. This latter compound is prepared by the reaction of 2-hydroxyethylhydrazine with diethyl carbonate in the presence of an alkaline metal catalyst and methanol:



N-(5-Nitro-2-furfurylidene)-3-amino-2-oxazolidone (Furazolidone)

In the first step (Figure 2), the solid alkaline metal catalyst is dissolved in methanol in a 10-gallon stainless steel, jacketed, agitated mixing tank (*7E*). The catalyst is fed through a hopper, and the methanol is pumped in from a 55-gallon drum. While these materials are heated to 78° C. to dissolve the catalyst, the methanol that vaporizes is condensed in a 10-foot-long reflux condenser and returned to the mixing tank.

The 2-hydroxyethylhydrazine, received in 55-gallon drums, is pumped from a weighed drum into the 100-gallon stainless steel, jacketed, agitated 3-amino-2-oxazolidone reactor (*8E*). Next, the diethyl carbonate, received in 55-gallon drums, is charged in a similar fashion. The reaction starts as soon as the solution of catalyst and methanol is added. The rate of addition is controlled to prevent an excessive temperature rise. The reactants are held at 75° C. for 2 hours with agitation. Any alcohol that distills off is returned to the reactor by a stainless steel reflux condenser (*5E*) that provides 30 square feet of cooling surface. At the end of 2 hours, the reactants are cooled to 20° C. The 3-amino-2-oxazolidone produced is not isolated.

At the start of the final reaction step to form furazolidone, tap water is added to the 300-gallon glass-lined, jacketed, agitated furazolidone reactor (*7E*); 94% sulfuric acid is then added from 12-gallon carboys. The 3-amino-2-oxazolidone solution is pumped into the reactor through a rotameter over a period of 1 hour. The 5-nitro-2-furaldehyde diacetate is then added from drums through a reactor hatch. Enough isopropyl alcohol is pumped in from a 12,000-gallon underground storage tank to form about an 8% solution.

The reactants are held at 75° C. for 1.5 hours. As the furazolidone, which readily precipitates, is cooled to 20° C., it is held in suspension by an off-center agitator used in combination with a baffle. The yield in this step is about 95 to 99%.

The product is filtered in a horizontal tank-type pressure filter (*4E*), 9 feet long and 36 inches in diameter and equipped with 29 vertical plates covered with 25 × 110 mesh stainless steel wire cloth. This unit, which provides a total surface area of 245 square feet, was selected for its ability to handle a wide variety of crystal types.

After the product is collected on the filter plates, it is washed with water until the pH of the effluent is about 6. The filter cake is then blown with compressed air to remove most of the water. If the cake is still too wet, it is partially dried inside the filter with hot air at about 80° C. The filter plates are then rolled out of the filter, and the product is dumped into a cart. From there, it goes to a 10-foot-long, 2-foot-diameter rotary dryer (*6E*), where it is dried with hot air at about 80° C. The product is collected in drums at the outlet of both the dryer and dust collector (*3E*). Both units are similar to those used in the preparation of the 5-nitro-2-furaldehyde diacetate. When necessary, the furazolidone is milled (*9E*) to pass through an 80-mesh screen. The final product is packaged in 15-pound drums.

Analytical tests are run on all raw materials and final products

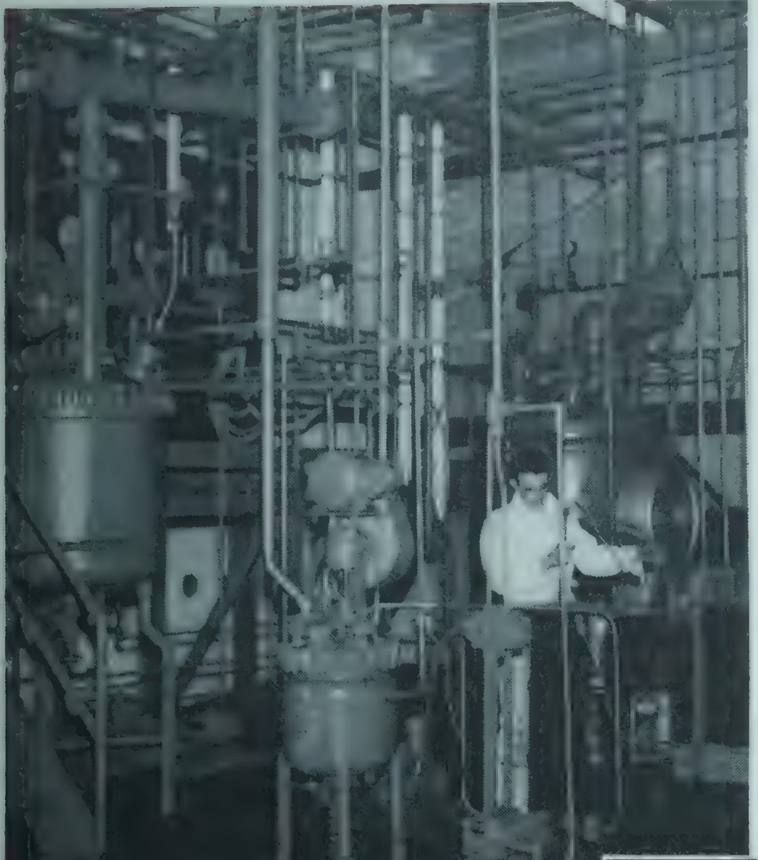
Each batch of nitrofurazone and furazolidone consists of 200 to 400 pounds of final product. The analytical laboratory tests all products, as well as all raw materials. The 5-nitro-2-furaldehyde diacetate is tested for melting point, color, and odor. Both the nitrofurazone and furazolidone are analyzed for melting point, color, odor, sulfate content, ultraviolet absorption, and pH of aqueous solution.

The nitrofurazone and furazolidone plants are adequately instrumented (*10E*) to ensure the accurate, automatic control of reaction temperatures. As an aid in employee training, effective use is made of graphic panel boards that illustrate the process steps involved.

The nitrofurazone and furazolidone plants are designed to produce one batch of final product in each 8-hour shift. The five nitrators perform two operating cycles in a single shift. At the current level of production, the nitrofurazone plant operates for two shifts a day, while the furazolidone plant is in operation one shift a day. On each shift, two men are required to handle the nitration step, two men the production of nitrofurazone, and two men the production of furazolidone. At all times, supervision is handled by a chemical engineer, who also supervises operations in the adjoining aspirin plant. On all shifts, a maintenance man is available to take care of emergency repairs. When needed, the more specialized types of maintenance work are performed by pipe fitters, electricians, instrument men, carpenters, painters, and other maintenance workers from the central shop.

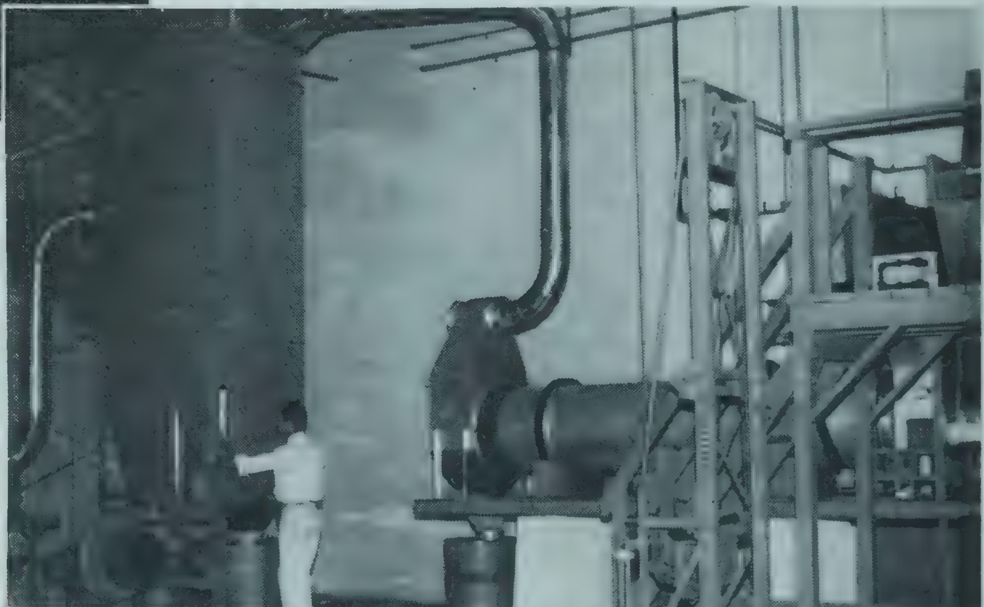
At present, investigations are in progress on improved methods of salvaging the by-product acetic acid, only about 60% of which is now recovered. Consideration is also being given to the bulk handling of nitric acid, which, although now purchased in drums, might be obtained more economically in tank cars.

Norwich produces its two other nitrofuran drugs, nitrofurfuryl methyl ether and nitrofurantoin, in a multipurpose pilot plant used previously in the development and early commercialization of nitrofurazone and furazolidone. In the preparation of nitrofurfuryl methyl ether, the first step is the synthesis of 2-furfuryl methyl ether from 2-furfuryl alcohol and methyl iodide in the



▲

Methanol is pumped into mixing tank in furazolidone plant; 3-amino-2-oxazolidone reactor is at left, furazolidone reactor at right

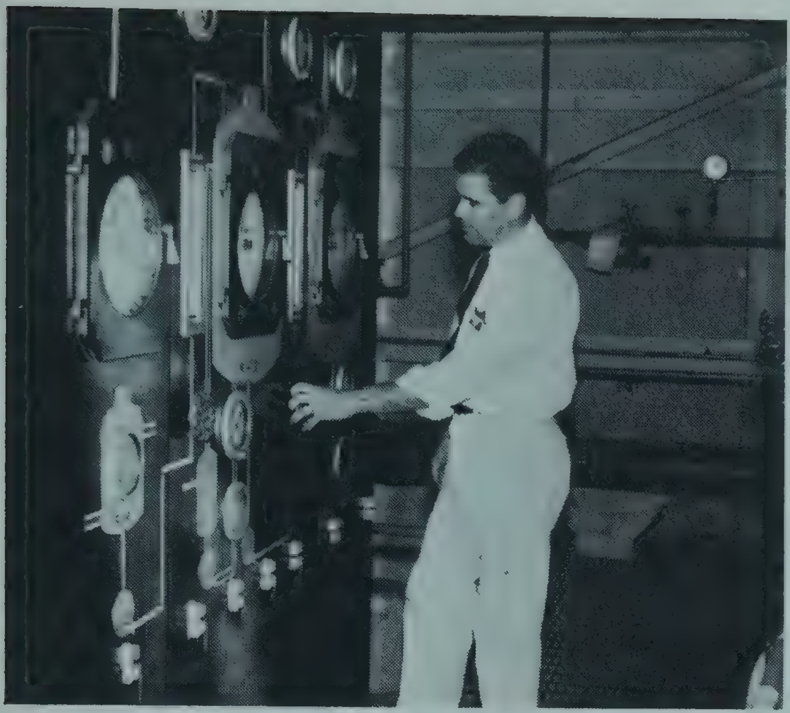


▲

Rotary drum dryer and dust collector are used in preparation of furazolidone; hoist lifts filter cake to dryer feed hopper

◀

Dried product is loaded into feed hopper of furazolidone mill; dust collector is shown at right



On the graphic panel board in the furazolidone plant are mounted various indicators, recorders, and controllers. The rotameters indicate the flow of liquids from one reactor to another

presence of a base. The product is nitrated to form an intermediate which, in the presence of a base, yields methyl 5-nitro-2-furfuryl ether (nitrofurfuryl methyl ether) and acetic acid.

The synthesis of nitrofurantoin begins with the reaction of monochloroacetic acid and hydrazine to form hydrazinoacetic acid. This product is treated with an alkali cyanate and a mineral acid to form 2-semicarbazidoacetic acid. The latter compound is subsequently reacted with 5-nitro-2-furaldehyde diacetate in the presence of acid to yield *N*-(5-nitro-2-furfurylidene)-1-aminohydantoin (nitrofurantoin), in addition to acetic acid and water.

Expanding markets are predicted for increasing number of nitrofurans

All evidence points to the further successful commercialization of the nitrofurans. The demand for both nitrofurazone and furazolidone is certain to increase as existing markets expand and new applications are introduced. So encouraging have been the results with nitrofurantoin that Norwich intends in the not-too-distant future to move its process out of the pilot plant and into new, large scale facilities.

As it has for the past 15 years, Norwich continues its intensive screening of new nitrofuran compounds. Under careful study are nitrofurans that possess physiological and pharmacological properties other than the antibacterial or chemotherapeutic properties commonly associated with these drugs. Work on these derivatives is currently in an early exploratory stage.

Norwich is also carefully testing the nitrofurans for possible use in agriculture. The demand for these compounds might be expanded tremendously if they could find effective, economical use in controlling bacterial or fungus diseases of fruit or vegetable crops.

The fact that the syntheses of nitrofurazone, furazolidone, and nitrofurantoin all involve the use of hydrazine or a derivative has given Norwich a valuable background in hydrazine chemistry. The company is currently exploring the potential applications for methyl, ethyl, and propylhydrazines, as well as other related compounds. Although Norwich has thus far concentrated its production efforts almost exclusively on medicinals, it is eyeing closely the possibility of branching out into the manufacture of specialty organic chemicals.

Meanwhile, Norwich's primary research emphasis is on the nitrofurans—compounds that represent one of the biggest medical discoveries since penicillin.

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Processing equipment

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(2E) Aluminum Co. of America, Pittsburgh, Pa., aluminum measuring egg, special; aluminum nitrators, special.
(3E) American Air Filter Co., Inc., Louisville, Ky., Amerjet dust collector, Model **6-100**.
(4E) American Machine and Metals, Inc., Niagara Filter Division, East Moline, Ill., horizontal pressure filter, Model **36H-245-3**; rubber-covered centrifuge.
(5E) Doyle & Roth Mfg. Corp., Brooklyn, N. Y., stainless steel condenser.
(6E) General American Transportation Corp., Process Equipment Division, Louisville, Ky., stainless steel rotary drum dryer.
(7E) Glascote Products, Inc., Cleveland, Ohio, glass-lined reactor, Data Sheet **801-26**; stainless steel mixing tank, special.
(8E) Pfaudler Co., Rochester, N. Y., glass-lined holding tank Type **VR 300**; glass-lined nitrofurazone reactor, series **R**; glass-lined receiving tank, Type **VR 50**; stainless steel crystallizer; stainless steel 3-amino-2-oxazolidone reactor; stainless steel semicarbazide reactor.
(9E) Pulverizing Machinery Co., Summit, N. J., Mikro-Pulverizer, Model **1SH**.
(10E) Taylor Instrument Co., Rochester, N. Y.
(11E) Wilcox Johnson Tank Co., Inc., Victor, N. Y., wooden nutsche filter.

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SALT MANUFACTURE

ALBERT S. HESTER, Assistant Editor

in collaboration with

HORACE W. DIAMOND
Morton Salt Co., Chicago, Ill.

SALT manufacture, not new nor based primarily on any chemical reaction, involves production of a large volume, low margin chemical; competitive operation calls for maximum exploitation of the present-day knowledge of chemical engineering. An evaporating plant, such as that of Morton Salt Co. at Manistee, Mich., must efficiently employ most of the unit operations to make a highly pure product with the lowest possible fuel and processing costs.

Since ancient times man has used salt in preparing and preserving food. Salt is essential to life and prehistoric man probably obtained it through his food just as animals do. No one knows when man first started to supplement his diet with sea salt, or with rock salt from the outcroppings forming "salt licks" frequented by his herds. It is likely that it followed soon after the adoption of the practice of cooking food, especially boiling, and thereby removing much of the salt. Earliest historical records of many civilizations show that salt was considered essential and a valuable commodity, and while today most countries are well supplied with salt, until comparatively recent times paucity of sources or poor transportation has given it a strategic importance affecting international relations.

Today the quantity of salt used in the United States for seasoning food is small compared to that used for other purposes. It is estimated that only about 4% of all salt produced is sold for table and household use, but eventually more salt finds its way into food indirectly through the food processing industries and through livestock feeding. Table I shows the distribution of U. S. salt consumption in 1952 (*17*).

Salt is found both in the sea, where being soluble it tends to collect, and in rock salt deposits formed when arms of the sea are cut off and conditions are favorable for evaporation. The sea is not only the source of the main constituent of rock salt, sodium chloride, but also is the source of the impurities, including the most troublesome one, calcium sulfate. All of the different salts found in sea water are found in rock salt, although solubility differences cause some fractionation during crystallization with resulting stratification of the deposits. In this process the most soluble salts, such as bromides and iodides, rarely crystallize and are almost never found in rock salt in any appreciable quantity. In addition to occurring extensively in oceans and as rock salt, salt is also found mixed with other constituents in certain rocks or dissolved in natural brines permeating porous rock and occasionally flowing out of the ground from salt springs. In the large salt domes of the Gulf region salt of sedimentary origin has been forced upwards toward the surface from great depths, perhaps 27,700 feet (*2*, *14*). This is possible because salt is somewhat plastic under extreme pressures.

Most refined salt is produced from artificial brines made by introducing water into a cavity in a rock salt deposit to dissolve the salt, and by pumping the solution to the surface. Brine, natural, artificial, or sea water, can be evaporated by heating or by solar methods. Evaporated salt (does not usually include solar salt) may be classified as either granulated or flake salt. Granulated salt consists of cubical crystals; flake salt, pieces of hopper crystals. Much brine is used directly without being evaporated, especially by the chemical industry.

Table I. Salt Sold or Used by Producers in United States, 1952

(By classes and uses in thousands of short tons)

Uses	Evap.	Rock	Brine	Total
Chlorine, bleaches, chlorates, etc.	527	907	3,817	5,251
Soda ash	[a]	[a]	7,195	7,195[a]
Dyes and organic chemicals	43	67	..	110
Soap (precipitant)	30	11	..	41
Other chemicals	118	603	[a]	721[a]
Textile processing	23	104	[a]	127[a]
Hides and leather	88	140	[a]	228[a]
Meat packing	344	420	..	764
Fish curing	20	11	..	31
Butter, cheese, and other dairy products	66	6	..	72
Canning and preserving	152	60	..	212
Other food processing	244	14	..	258
Refrigeration	76	143	[a]	219[a]
Livestock, agr., and gen. farm use[b]	777	305	..	1,082
Highways, railroad, dust and ice control	17	800	..	817
Table and other household use	468	78	..	546
Water treatment	282	338	[a]	620[a]
Metallurgy	35	71	..	106
Undistributed[c]	332	489	324	1,145
Total	3,642	4,567	11,336	19,545

[a] Data included with undistributed in order to avoid disclosure of individual company operations.

[b] Livestock salt is about 90% of total.

[c] Comprises miscellaneous uses and uses for which data may not be shown separately (see footnote [a]), including some exports and consumption in territories and possessions.

In the United States in 1951 there were 48 salt evaporating plants (including solar evaporation installations) scattered through 13 states and Puerto Rico. There were 18 rock salt mines in eight states and 17 brine production operations distributed among seven states (*6*). U. S. production in 1952 was 19,202,037 short tons; world production was estimated to be 54,000,000 tons (*16, 17*).

The literature of salt manufacturing technology is extensive, although the most detailed work on the subject is somewhat out of date (*11*). Much valuable material is included in some of the general books on the chemical industry (*1, 9, 13*) and two articles describe particular plants and processes (*7, 8*). At least one nontechnical work on salt has been published (*4*); this book contains many references concerning the history of the salt industry. Probably the most extensive treatment of solar salt is given by Tressler (*15*).

Morton Manufactures Salt in Each Major U. S. Producing Area

The Morton Salt Co., an outgrowth of a salt sales agency founded in 1848, manufactures salt in nine different plants in the United States. In addition, a subsidiary at Inagua in the Bahamas produces solar salt for the coastal markets. To reduce transportation costs to a minimum, the company has located plants in each major salt producing area.

Morton produces salt by mining, solar evaporation, and steam evaporation. The methods used at the various plants are determined by natural resources of the area, and by geological and climatic conditions. In most areas both rock and evaporated salt are produced—evaporated salt being a refined product that commands a premium price. Rock salt is produced where there are suitable deposits and markets for a low-cost salt that may contain considerable insolubles. Solar salt is normally produced in areas having no rock salt, such as the West Coast and at Great Salt Lake.

The different salt products manufactured by Morton are numerous. Rock salt is sold as "run of the mine," or like solar salt, as one of several screened grades varying in size down to table salt fineness or smaller. Granulated salt is sold as air dried salt direct from the vacuum pan, or as dried and screened salt for table and flour salt grades, and some is ground as fine as 85% −325 mesh. There is a series of compressed salt products which includes 50-pound blocks for cattle feeding, made from salt from any source, and pellets for water softening and salt tablets 10 to 400 grains in size made from evaporated salt. Grainer, or flake, salt is screened to obtain specialty salts such as those used for cracker topping and prepared flour. A host of additives increases the number of different products. Of special interest is a rock salt treated with small amounts of phosphate and carbonate so that it produces a pure brine when dissolved. Addition of potassium iodide to table salt to correct deficiencies of iodine in human diets has been practiced for a long time and recently this program has been expanded to include, in addition to iodine, trace elements, such as copper, cobalt, iron, manganese, and zinc, required by farm animals. A salt containing 22% calcium sulfate is used for "firming" tomatoes; sodium phosphate added to salt prevents the formation of struvite (ammonium magnesium phosphate) crystals in fish products; and paraffin incorporated into salt tablets allows them to dissolve slowly when swallowed to keep the body salt content at a satisfactory level during exposure to excessive heat. Corrosion inhibitors are added to salt used for freeze proofing coal and antioxidants are added to salt for potato chips. There is even a salt toothpaste. These supply only a partial list of the vast array of salt products which the company markets.

The Manistee, Mich., plant of the Morton Salt Co. was built in 1923. Its production capacity of over 1000 tons per day makes it the largest evaporated salt plant in the United States. The location of Lake Michigan enables it to transport salt by ship to any part of the Great Lakes region. It is also conveniently located for rail and truck shipments to heavily populated centers.

The first well in the Manistee area was drilled in 1879 with the

Raw material is removed from underground salt deposits by brine wells

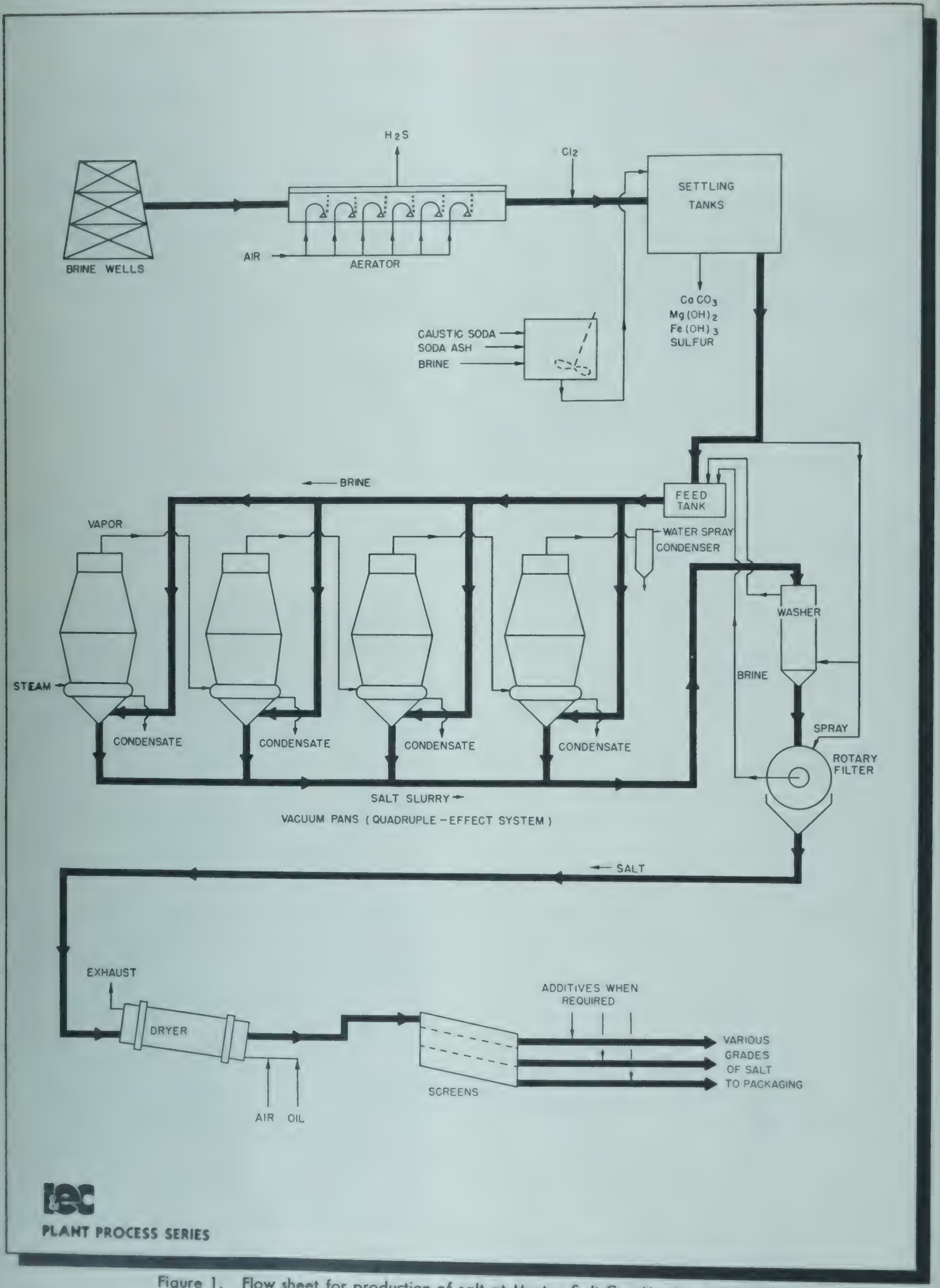

H$_2$S
Cl$_2$
SETTLING TANKS
BRINE WELLS
AIR
AERATOR
CaCO$_3$
Mg(OH)$_2$
Fe(OH)$_3$
SULFUR
CAUSTIC SODA
SODA ASH
BRINE
BRINE
FEED TANK
VAPOR
WATER SPRAY
CONDENSER
WASHER
STEAM
BRINE
CONDENSATE
CONDENSATE
CONDENSATE
CONDENSATE
SPRAY
ROTARY FILTER
SALT SLURRY
VACUUM PANS (QUADRUPLE-EFFECT SYSTEM)
SALT
EXHAUST
ADDITIVES WHEN REQUIRED
DRYER
VARIOUS GRADES OF SALT TO PACKAGING
SCREENS
AIR
OIL
I&EC
PLANT PROCESS SERIES

Figure 1. Flow sheet for production of salt at Morton Salt Co., Manistee, Mich.

hope of finding petroleum or natural gas (*3*). Although disappointed in not finding either of these materials, the drillers discovered that the salt beds underlying much of Michigan extended to Manistee, and the availability of fuel in the form of scrap wood from the declining local lumber industry made the establishment of a salt industry highly practical. After the first well a number of salt companies erected plants burning scrap wood to heat their evaporating pans. Today only two plants remain in the area, and coal is used for fuel.

Since the end of World War II several million dollars have been spent on the modernization of Morton's Manistee plant. Improvements include a new boiler capable of operating at a pressure of 700 pounds per square inch, modernization of the grainer plant, conversion of one of the evaporators from triple to quadruple effect, and installation of completely automatic machinery for packaging table salt for household use.

In addition to its sodium chloride facilities, the plant also includes a factory for making reagent grade sodium, potassium, and ammonium bromide from a chemical brine occurring at a level below the main salt bed. Magnesium from this brine, augmented by additional magnesium from dolomite, is used in production of the magnesium carbonate, an additive used in table salt.

Construction and Operation of Brine Wells Are Highly Specialized

Brine for evaporating plants is obtained usually by hydraulic mining, through wells reaching down into the rock salt. A well is usually constructed to contain two concentric strings of pipes in order that water to dissolve the salt can be introduced through the annular space and brine can be removed through the central tube opening at some different level. After adjacent wells have been operated for 1 or 2 years, the developed cavities become connected. When this occurs the usual practice is to introduce water through one well and remove brine through another.

The problem of producing a saturated brine is usually encountered only in the development of a new brine field. Once the cavity, which develops around the bottom of a well in the salt bed, has reached the size normally attained after operation of a year or two, then saturated brine at a rate of 200 gallons per minute can be obtained in a salt bed 10 to 20 feet thick. In developing the cavity of a new brine well, the method of operating the well can determine, to a certain degree, the shape of the cavity, and thus have an important effect on both output and maintenance. For a high capacity well the cavity should expose a large area of salt surface to the dissolving action of the water, but should have such a shape that the roof does not collapse. Large blocks of material falling to the bottom of the cavity may break the pipe and smaller debris may block the tube opening, or become cemented to the tube by crystallization, and eventually settle and break the tube.

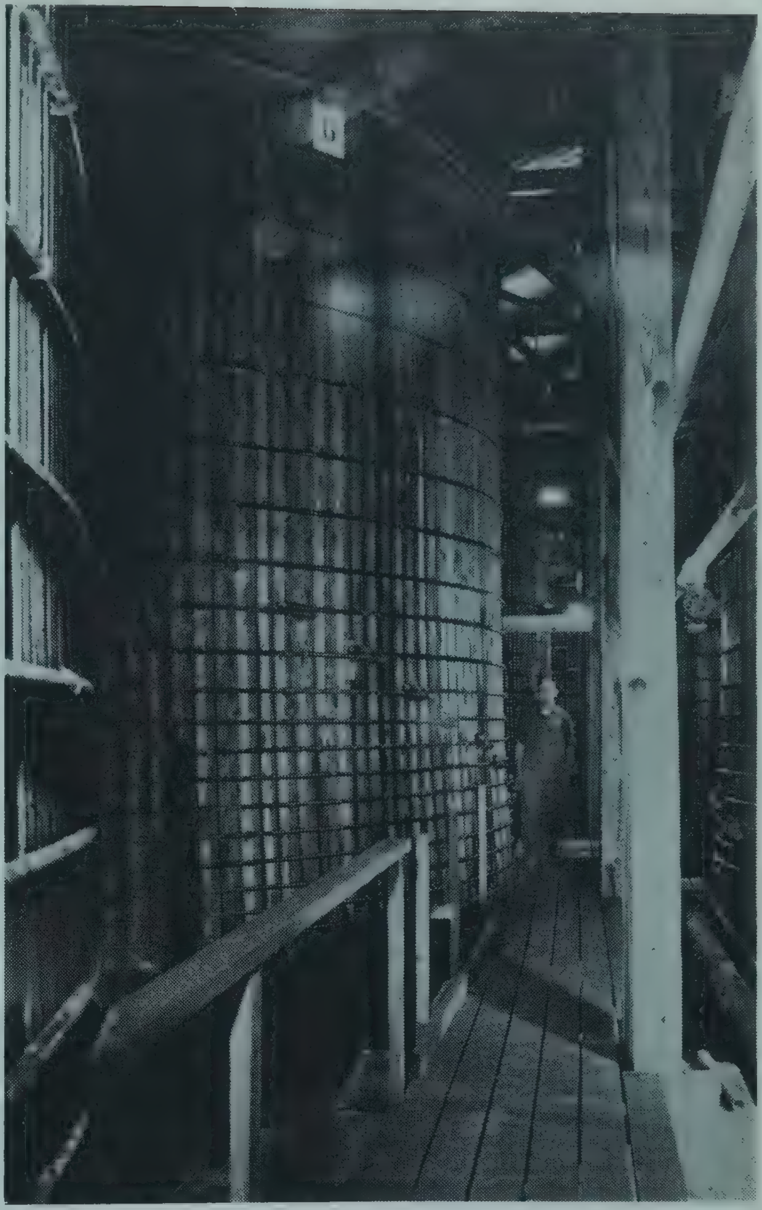
All methods for preventing the caving of the roof involve one of the following:

1. Salt can be withdrawn from the cavity at a point removed from the tubing, so that any roof caving will not involve the tubing. This is usually accomplished by the use of two connected wells, one for introduction of water and the other for removal of brine. The undercutting of the salt bed so that the two wells become connected together by a channel at the bottom of the bed establishes the initial connection with the smallest possible cavity around the introducing well. This undercut can be made by the use of oil or air in the cavity to protect salt in the upper part of the bed from the dissolving action of the water.

2. Development of a cavity with a small diameter will give a roof of minimum area and consequently reduce caving tendencies. The diameter can be controlled by the method used in introducing the water into the cavity. If water is introduced at the roof and brine is drawn off at the floor, a cavity with a "morning glory" shape is obtained, producing a maximum area of exposed roof and resulting in the greatest amount of caving difficulty. The shape of the cavity can be made cylindrical with a roof of minimum area by introducing the water into the bottom of the cavity and withdrawing brine near the roof. However, because water is lighter than brine and tends to rise to the roof of the cavity, the flow must be restricted to a small fraction of that used with the other method of injection to maintain a saturated brine flow.

3. Extra strong steel tubing which will not be broken by any roof caving is sometimes used. This practice is applicable if the characteristics of the roof are such that it tends to slough off in small pieces.

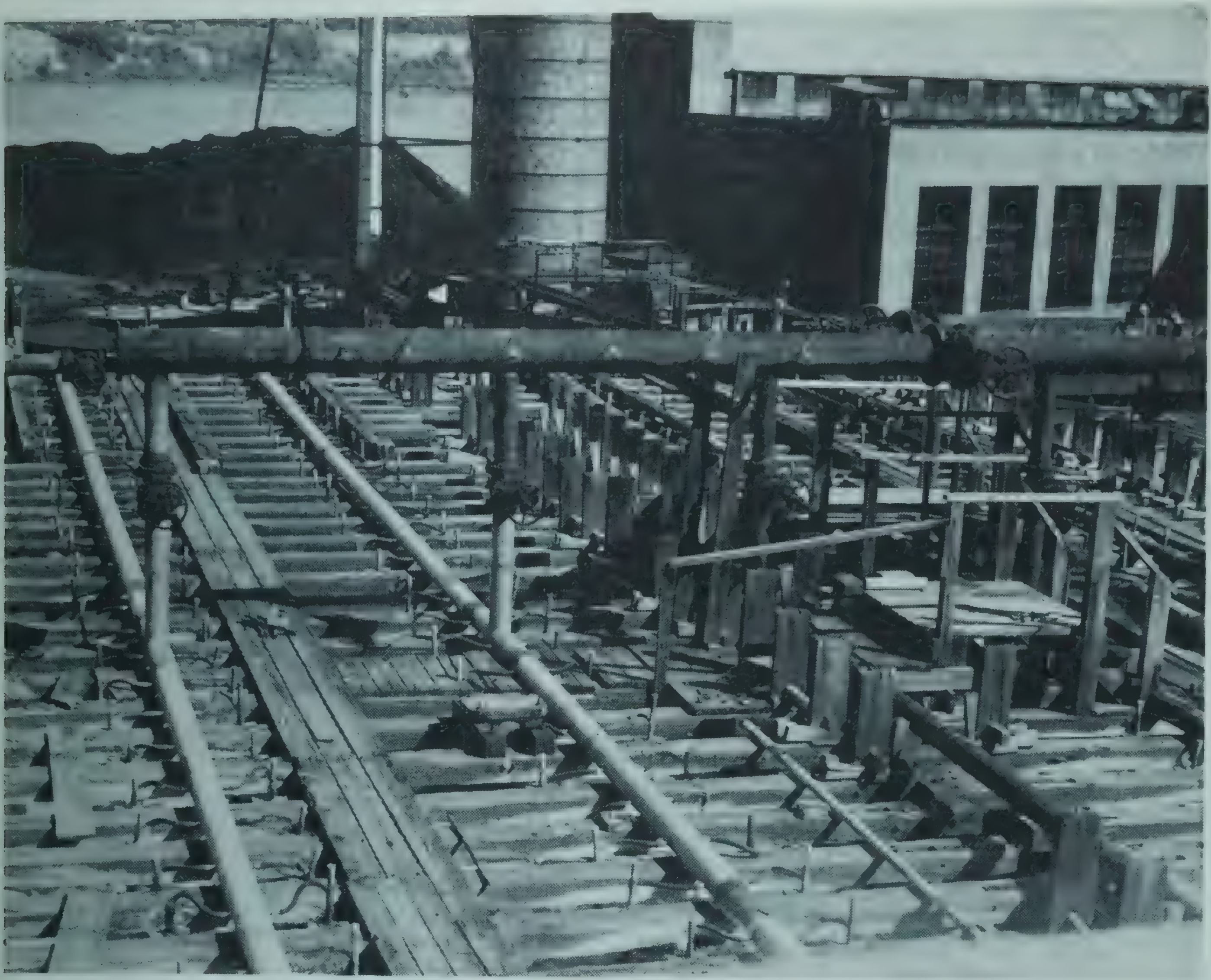
4. Use of plastic tubing for brine wells is a rather new practice. If large areas of roof tend to cave at the same time no pipe will be strong enough to survive and plastic pipe can be broken easily during the drilling necessary to clean the hole.



Impurities in raw brine from wells are allowed to settle out in these tanks

The Brine Must Be Purified before Use

The brine from which salt is produced varies widely in chemical composition. In some cases, the salt may be produced directly from the brine without purification, but in most cases some treatment of the brine is required. Impurities found in brine include calcium, magnesium, sulfates, traces of hydrogen sulfide, bicarbonates, and ferrous iron. The source of these impurities is found in either the salt deposits or the dissolving water, that which is pumped into the cavity or subterranean water that flows naturally into the salt cavity as brine is removed.



Brine tanks where air is blown through brine to remove certain impurities

The treatment given brine for the removal of the calcium, magnesium, and sulfate impurities depends upon the purity required in the final product; hydrogen sulfide and iron must be removed in all cases because of the possible effect upon the quality of the product. Calcium, magnesium, and sulfates may be removed either by batch or continuous treatment in equipment of the accelerator type which eliminates calcium carbonate supersaturation. Calcium carbonate causes scaling on the evaporating heating surfaces. Where the composition of the brine varies widely control of the brine treatment can best be obtained by batch treatment.

Morton's Manistee Plant Obtains Brine from Ten Wells

Brine from the Manistee plant is obtained from 10 wells sunk into a bed of salt 20 feet thick about 2000 feet beneath the surface. Surface driven deep well pumps are used to bring it to the surface. Submerged pumps, and airlift and water pressure injection methods are employed at some other installations. The maximum flow of brine obtained from any well at Manistee is 200 gallons per minute, about average for the industry, where the flow range is from 10 to the over 800 gallons per minute, obtained from the extremely large cavities which can be developed in the salt domes in the South, where salt deposits are several thousand feet thick.

Table II. Impurities in Saturated Brine from Manistee Wells

	Impurities, Grams/Liter	
	Untreated	Treated
Na_2SO_4	..	5.40
$CaSO_4$	5.50	6 p.p.m.
$MgCl_2$	0.75	
$CaCl_2$	0.30	—
H_2S	0.15	..
$MgSO_4$	..	0.05
Na_2CO_3	..	0.4

Analyses of the saturated brines from Morton's Manistee wells are shown in Table II.

Some salt brines used at other plants do not contain hydrogen sulfide, but, at Manistee, the first step in purification starts when brine from the wells flows through a shallow wooden tank, 20 feet wide, 150 feet long, and 4 feet deep, which is aerated to remove most of the hydrogen sulfide (Figure 1). Baffles are placed so that the brine flows in a zigzag course along the full length of the tank and returns along the other side to discharge at the same end. At intervals a few feet apart, air supplied by two blowers of 5500 cubic feet per minute and 55 horsepower, is introduced below the surface of the liquid through inverted funnels having notched edges to break up the air into small bubbles.

A small stream of chlorine is introduced into the brine stream as it passes through the line carrying it from the aeration tank to the settling tanks. The chlorine oxidizes the last traces of hydrogen sulfide (hydrogen sulfide content at this stage is 0.007 gram per liter) to free sulfur which will settle in the settling tanks. Chlorine also oxidizes the ferrous ions so that iron is precipitated as ferric hydroxide. A test with lead acetate paper determines whether any hydrogen sulfide remains. The settling tanks are 90,000-gallon cypress tanks 25 feet in diameter and 30 feet high and are placed indoors. Manistee has 20 of these tanks with a total settling capacity of 1000 gallons per minute. After settling, the brine is ready for evaporation. Some calcium sulfate and lesser amounts of magnesium chloride remain in the brine. Most calcium sulfate is removed later in the process, but to produce a salt essentially free from calcium and magnesium the brine must be treated with soda ash and caustic soda. These chemicals are made into a slurry by mixing 3900 pounds of soda ash and 600 pounds of caustic soda with brine. Mixing of the slurry and brine in the settling tank is accomplished by a 30-minute period of aeration through a cross-pipe sparger and settling is normally completed in 24 hours. Titration with 0.1*N* hydrochloric acid shows whether the proper amount of soda ash has been added. A 100-ml. sample of a satisfactory brine requires 2.5 ml. of acid to reach an end point with phenolphthalein and 5.0 ml. with methyl orange. The purified brine is then drawn off through an 18-inch standpipe and the settled material containing the iron, sulfur, magnesium, and part of the calcium impurities is flushed out with water and discarded to prepare the tank for a new batch. In plants where the brine has a low hydrogen sulfide content, the aeration tank step and chlorine treatment are omitted; hence, aeration is not required.

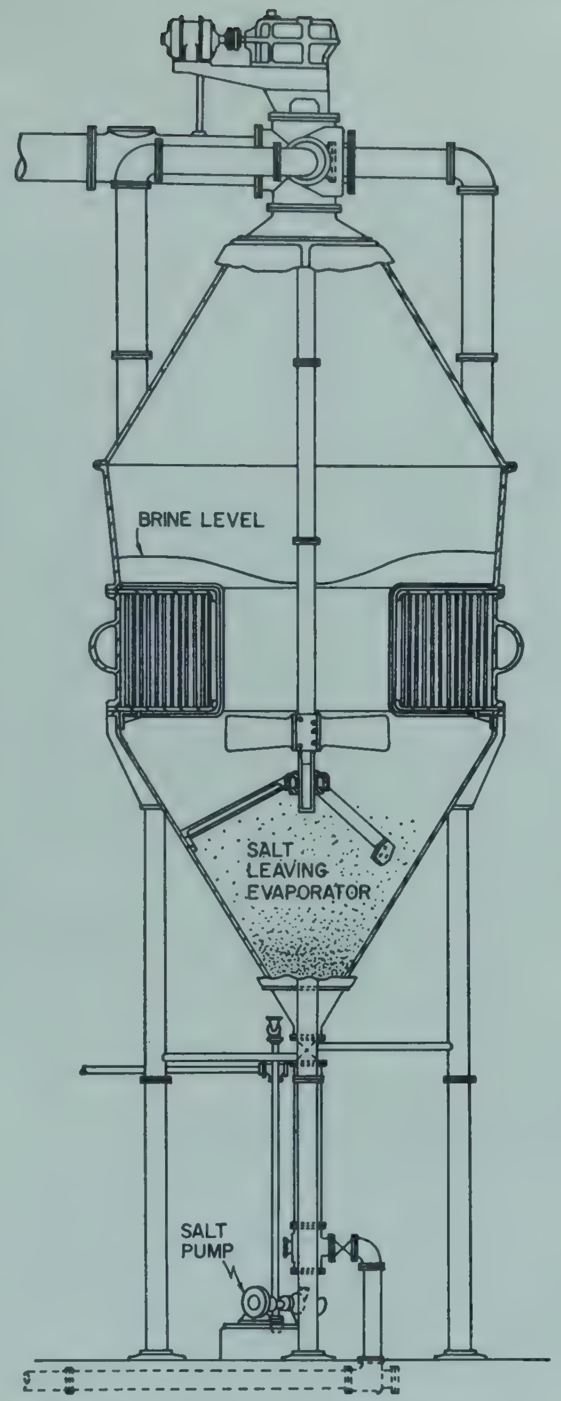


Figure 2. Schematic drawing of a vacuum pan

Table III. Some Operating Conditions for Triple Effect Evaporator

Steam to first effect: 54,000 lb./hr., 220° F.
Total production: 21 tons/hr.

	Temperature, ° F.				
Effect	Brine	Mean[a]	Boiling point rise	% of Salt Made	Brine Level, In. above Calandria
1	200	20	17.3	38.9	22
2	159	23.7	16.4	32.5	18
3	114	28.6	15	28.6	13

[a] Mean temperature is difference between steam and boiling liquid.

Multiple Effect Evaporators Are Used for Vacuum Pan Salt

At Manistee about 90% of the salt output is made by the vacuum pan process, the remainder by the grainer method. In the vacuum pan process, the salt is crystallized in multiple effect vacuum evaporators from a boiling brine, a process which normally yields fine cubical crystals of −20 to +100 mesh, ideal for table salt and many food processing operations.

At Morton's Manistee plant vacuum pan evaporation facilities consist of seven large pans arranged to make one triple effect and one quadruple effect evaporator. Construction of one of these pans is shown in Figure 2. Steam introduced into the calandria heats the brine which rises through the tubes and circulates down through the circular downtake by natural convection aided by mechanical agitation. The body and tube sheets are cast iron and the tubes are copper. Diameter of the pan at the calandria is 18 feet and the downtake tube is 8 feet 10 inches in width. There are 2240 tubes, each having an outside diameter of 2.5 inches and a length of 4.5 feet. Total heating surface is 6600 square feet. The agitator is 8 feet in diameter, has four blades with a pitch of 12 feet 6 inches, and rotates at 36 r.p.m.

Vapor from each effect passes to the calandria of the next effect except vapor from the last pan which goes to a barometric plate condenser. Noncondensable gases are vented to the condenser from each effect.

Brine is fed continuously to the pans in parallel with the introduction being into the bottom section of each pan. Table III lists some of the operating conditions for the triple effect evaporator and Figure 3 is a material balance for the evaporators. Temperature affects the viscosity and the heat transfer coefficient, as shown in Figure 4.

Centrifuges dewater the flake salt

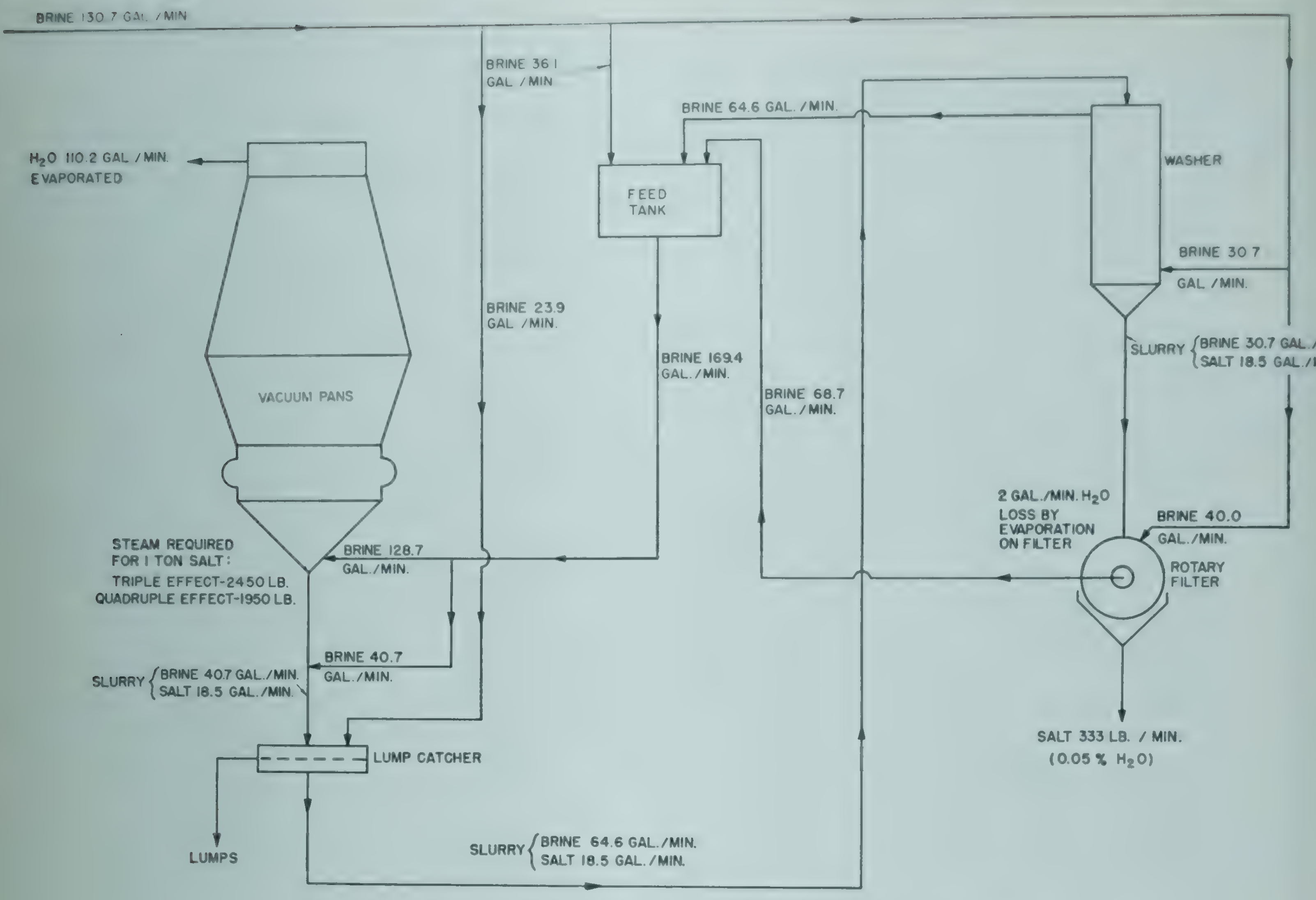

BRINE 130.7 GAL./MIN
BRINE 36.1 GAL./MIN
H_2O 110.2 GAL./MIN. EVAPORATED
BRINE 64.6 GAL./MIN.
FEED TANK
WASHER
BRINE 30.7 GAL./MIN.
BRINE 23.9 GAL./MIN.
BRINE 169.4 GAL./MIN.
SLURRY { BRINE 30.7 GAL./MIN. SALT 18.5 GAL./MIN.
VACUUM PANS
BRINE 68.7 GAL./MIN.
2 GAL./MIN. H_2O LOSS BY EVAPORATION ON FILTER
BRINE 40.0 GAL./MIN.
STEAM REQUIRED FOR 1 TON SALT:
TRIPLE EFFECT-2450 LB.
QUADRUPLE EFFECT-1950 LB.
BRINE 128.7 GAL./MIN.
ROTARY FILTER
BRINE 40.7 GAL./MIN.
SLURRY { BRINE 40.7 GAL./MIN. SALT 18.5 GAL./MIN.
LUMP CATCHER
SALT 333 LB./MIN. (0.05 % H_2O)
LUMPS
SLURRY { BRINE 64.6 GAL./MIN. SALT 18.5 GAL./MIN.

Figure 3. Material balance for 10-ton-per-hour vacuum pan system

Salt crystals formed in the boiling brine remain in suspension until they grow large enough to sink to the bottom where they are continuously drawn off as a slurry by a centrifugal pump. The slurry passes through a screen with $^1/_2$-inch holes to remove lumps that might lodge in the piping system and throw the system out of balance by altering the flow rate. Once the slurry valve is properly set it will operate for hours without attention so one man can control salt removal from all seven pans.

The mother liquor in the slurry contains calcium sulfate in solution or in the form of a fine suspension, obtained by carefully controlling conditions in the pan. Suspended particles are removed by washing the salt with fresh brine which is then added to the evaporator feed at the feed tank provided to collect the brine streams from the various salt washing operations. Therefore calcium sulfate builds up inside the vacuum pan and when this becomes excessive the evaporator must be closed down and drained. A small amount of pan brine containing calcium sulfate is returned to the evaporator when it is started again. These calcium sulfate nuclei form growing surfaces in the evaporator upon which calcium sulfate is deposited in preference to the surface of the tubes.

There is one washer, a 6-foot diameter conical-bottom tank, approximately 15 feet in height, for each set of evaporators. Slurry enters the top and brine flows countercurrent from bottom to top. Hydraulic classification takes place and the calcium sulfate is carried out the top with the brine while salt falls to the bottom. As mentioned above, the overflow brine is sent back into the evaporator. Washed salt flows from the conical bottom of the washer onto a rotary vacuum filter *(9E, 11E, 14E)* for dewatering. The filter cake is washed with a spray of brine which is also returned to the evaporator via the feed tank.

For many years filter parts coming in contact with process material were made of cast nickel alloy. More recently filters have been fabricated from welded type 316 ELC stainless steel plates. Corrosion resistance is better, and the cost of machining the castings has increased, making fabrication from plates cheaper.

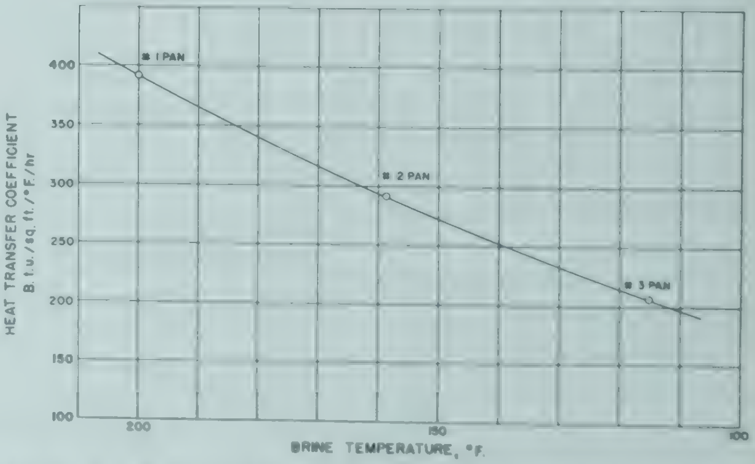


Figure 4. Relationship between brine viscosity and heat transfer coefficient

The top feed filter used at Manistee is the conventional method of dewatering, but continuous centrifugals may also be used. Both types of equipment are satisfactory and the decision on selection is dependent on power costs. If power is expensive, centrifugals can be justified.

Salt Evaporation Has Many Special Problems

Besides the general problems of maximum utilization of heating surface and power, and reduction of entrainment, special problems are involved in designing and operating salt evaporators of the calandria type, the most universally used. The foremost problem is the production of salt having the desired crystal size and purity. Crystal size is affected by the amount of circulation in the pans, the quantity of salt suspension in the pan brine, the location and type of propeller, and the extent of separation of proper sized salt crystals by classification in the conical bottom of the pan. The relationships between these factors vary from plant to plant; industry practice has been to adopt a standard pan design but to vary operating conditions, such as circulation and salt held in suspension, in order to obtain the product desired. In general, however, the industry does not have a simple means whereby particle sizes of granulated salt can be varied over wide limits. This inability to change particle size distribution by some alteration of operating conditions becomes especially troublesome in the case of the finer grades of salt where the market demands fluctuate.

The purity of salt is largely determined by how effectively the calcium sulfate can be eliminated by washing. Some separation is made by classification in the pan cone, since most of the calcium sulfate is less than a micron in size, but a small portion becomes occluded in the salt crystals, while another portion grows to the size of the salt crystals, making complete separation impossible.

A more recently adopted type of evaporator than the older design cone-bottom pans with calandrias having center downwells for circulation by a propeller is the evaporator with an external heat exchange and a pump for circulation. Both types of equipment give satisfactory results. The poor circulation that was characteristic of the old calandria pans is overcome with the development of more efficient propellers with integral straightening vanes which are made both in Europe and the United States (*3E, 16E*). With these propellers just as effective utilization of heating surface can be obtained as that with a pump so it is possible to take advantage of the saving in power inherent to the calandria type pan. The main advantages of the outside heat exchanger type are the greater accessibility of the pump and heater for repairs.

A significant modification of the heat exchanger evaporator is the Oslo evaporator in which the rate of crystal nuclei formation can be controlled to produce a very coarse salt, −10 to +20 mesh, if desired.

In Europe multiple effect steam economy is obtained in equipment of unique design. Brine is heated in a series of heaters supplied with vapor by an equal number of flash evaporators. In each of these flashers the brine is cooled by flashing approximately 10° to 20° F. and is raised in temperature a corresponding amount in the heater receiving vapor from the flasher. The final heater is supplied steam from a boiler and vapor from the last flasher goes to a condenser. By this method of operation only one boiling point rise needs to be deducted in determining the effective temperature drop of the system between boiler steam temperature and condenser. This makes possible an almost unlimited number of effects. In actual practice installations, in which as many as ten effects are in use, make possible a great economy in steam.

In this country a process has been developed for making evaporated salt from rock salt with very small steam consumption (*12*). Advantage is taken of the fact that calcium sulfate is much less soluble in brine at 225° F. than it is at 180° F. A mixture of rock salt and recycled brine from a later step in the process is heated to 225° F. The brine becomes saturated with both salt and calcium sulfate. Because calcium sulfate is much more soluble at the 180° F., the brine is flash cooled to this temperature in the evaporator so it cannot crystallize out with the salt.

The characteristic crystal formation of salt produced in evaporators is a cubical grain. For certain uses, a salt having greater surface area and less bulk density is required, such as salt produced in the grainer pans described later. The grainer process for producing salt is more expensive than the vacuum pan process, and it is desirable to produce a grainer type of salt in vacuum pans. This development has been partially realized in England, where a dendritic salt is obtained by the addition of small amounts of potassium ferricyanide to the brine, changing the crystal habit of sodium chloride (*10*).

The materials of construction in evaporators used in the salt industry have, up to the present time, been almost entirely cast iron bodies and tube sheets and copper tubes. Cast iron has given extremely good service, for many of the vacuum pans operating today have been in service for many years. Some success was obtained by covering with rubber those parts subjected to rapid erosion, such as propellers and shaft. Concrete linings for the pan bodies are also effective. Cast iron evaporators have been subject to some maintenance troubles especially with the tube sheets and tops of the pans which have to be renewed periodically because of corrosion. The product of this corrosion is iron oxide in the form of small particles which may appear in the salt and affect its salability. Because of this difficulty, all new vacuum pan installations will probably be constructed with nonferrous materials in contact with the brine.

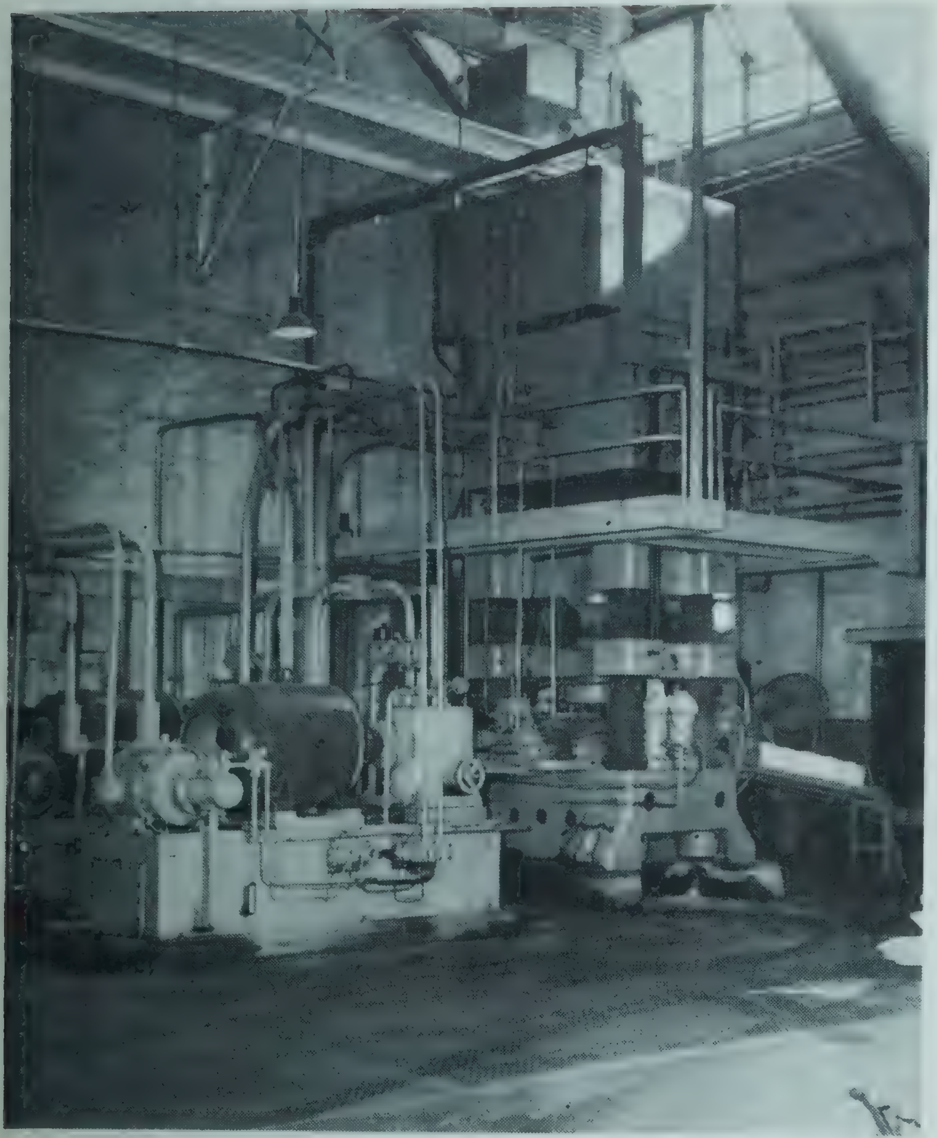
Considerable progress has been made through the years in the operation of salt evaporators. The most outstanding advance was the extension of the time of operation between tube scalings and boiling out to remove salt incrustation. Only a few years ago, weekly drilling of the tubes was required for removal of scale (calcium sulfate), and boil-outs with fresh water to remove incrusted salt were a daily routine. At the present time, pans can be used for years without scale accumulation on the tubes, and continuous operation of the pans for one week is possible without salt incrustation becoming excessive. These improvements were made possible by understanding the causes of scaling which are associated with the calcium sulfate and salt supersaturation in the pans. Scaling is avoided by providing sufficient salt and calcium sulfate suspension to reduce supersaturation to nonscaling levels. Suspensions of 20 grams per liter are adequate.

Other improvements in the operation of the pans have resulted from instrumentation. The use of level controls is now standard practice. Instruments for recording and controlling salt suspension in the pans are also being used. The salt suspension is proportioned to the pan brine density which is measured by a differential pressure cell. A correction must be made for density changes due to variation in the calcium sulfate suspension in the pan brine. In evaporators operating on brine of uniform composition, the salt concentration in a slurry flowing through a line is now measured in some plants with instruments that determine the energy absorption from a radioactive material. This affords a means of constantly withdrawing salt from the pans.

Effective capacity of existing evaporators was also increased by increased steam pressures. Recently by using steam at 50 pounds per square inch in the first pan the over-all temperature drop necessary for a quintuple effect evaporator was obtained by N. V. Koninklijke Nederlandsche Zoutindustrie in The Netherlands.

A good deal of experimental work has been done on a submerged combustion process. Texas Brine Corp. in Houston operated a submerged combustion unit for several years which produced experimental quantities of a high quality salt. Starting with raw brine containing 99.25% sodium chloride (principal impurity, calcium sulfate and some magnesium chloride), the firm was able to manufacture salt having a fine texture by direct heating with natural gas.

Submerged combustion units permit a lower initial investment, compared with vacuum pan equipment, but the long term increase of natural gas prices makes the process appear less favorable now than it was a few years ago. Texas Brine decided to



Block press prepares salt in block form for cattle feeding

explore the possibilities of submerged combustion because the process looked attractive from the standpoint of lower first cost; unlike conventional pan evaporation, the new method would not require a power plant to generate steam, and the brine could be processed without chemical treatment to remove impurities.

Since calcium sulfate scaling no longer presents a problem in vacuum pans, elimination of this by use of submerged combustion is of no particular advantage. However, the magnesium chloride in brine is converted to carbonate by the carbon dioxide produced in the submerged combustion process. Since magnesium carbonate is added to the salt anyway, and its presence in the brine is not detrimental, a means is provided for cheap addition of this material to the finished product.

Submerged combustion has a high heat efficiency, but it is really no more than a single effect evaporation. Even though exhaust heat from the combustion process can be utilized to operate auxiliary crystallizers needed to promote crystal growth, rising natural gas prices tend to favor the economics of multiple effect evaporators.

Texas Brine is currently working on a different type of evaporator, which is neither a true vacuum pan nor a submerged combustion unit, but one that incorporates a combination of both operating principles.

Dewatered Salt Must Be Dried, Screened, and Packaged

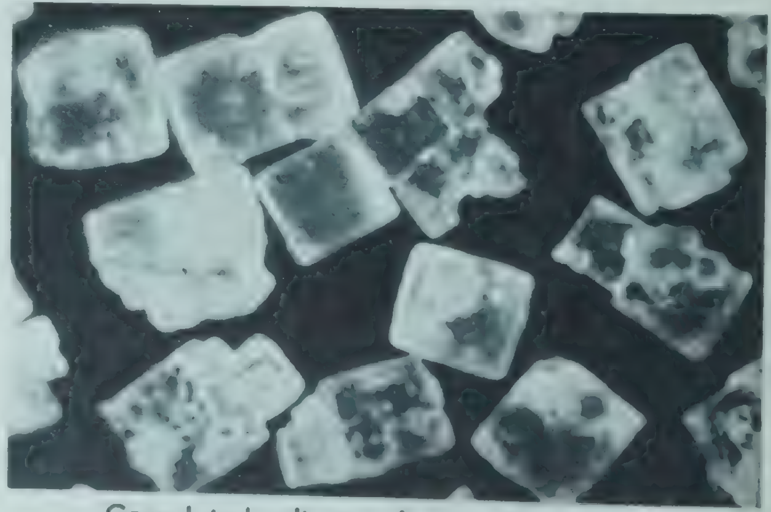
The salt from the filter moves to the dryers by conveyor belt. The conventional equipment for drying salt is the rotary kiln. At Manistee the two kilns are oil fired and lined with type 316 stainless steel.

Many recent developments in salt drying equipment have advantages over rotary dryer methods. A dryer containing a fluidized bed of salt is described in the literature (*5*). Air is preheated by passing through a fluidized bed of hot salt which is cooled simultaneously. Preheated air is further heated in a heater and sent through the second fluidized salt bed where drying takes place. Salt slowly passes from the drying to the cooling bed from which it is withdrawn. This dryer is claimed to have the advantage of producing a dry salt at a lower temperature with one third of the usual drying fuel cost. The low temperature of dried salt is desirable in order to prevent subsequent caking of the dry salt in storage. This phenomenon is associated with the liberation of occluded moisture when the salt is held at high temperatures in the bins. The stack dryer is also in use. In this equipment salt is dried either as it falls by gravity through a stream of hot air or is carried through the dryer with the air. This type of equipment produces a cooler salt than the rotary dryer because of the short contact time between salt and hot air.

The salt from the dryer goes to the screens (*2E, 13E, 15E*). A number of particle size separations are made: The finest grade is a flour salt; the next coarsest is table salt; and the coarsest size is industrial salt. Many types of screens are satisfactory for screening granulated salt, but it is necessary to use a screen subject to sharp impacts, otherwise the square meshes in the screen will be blinded with the cubical grains of salt.

Following size separation the salt is either packed directly or blended with various additives to obtain salt products for many special purposes. Because of its particle size the salt mixes well with many ingredients without segregation. The mixing of these additives with the salt is usually done on a continuous basis using gravimetric feeders (*4E, 10E*) and mixing screw conveyors (*5E, 7E*). In order to get the additives to adhere to the salt crystals, thorough mixing is required. This can be obtained in screw conveyors with cut flights.

The property of salt to absorb moisture at relative humidities frequently prevailing presents a number of problems to the industry. Because of moisture absorption, salt may cake or lose its free flowing properties. For some purposes, such as table salt, both caking and dampness of the salt are undesirable, while for certain uses, caking is the only consideration. Two ways



Granulated salt crystals magnified greatly

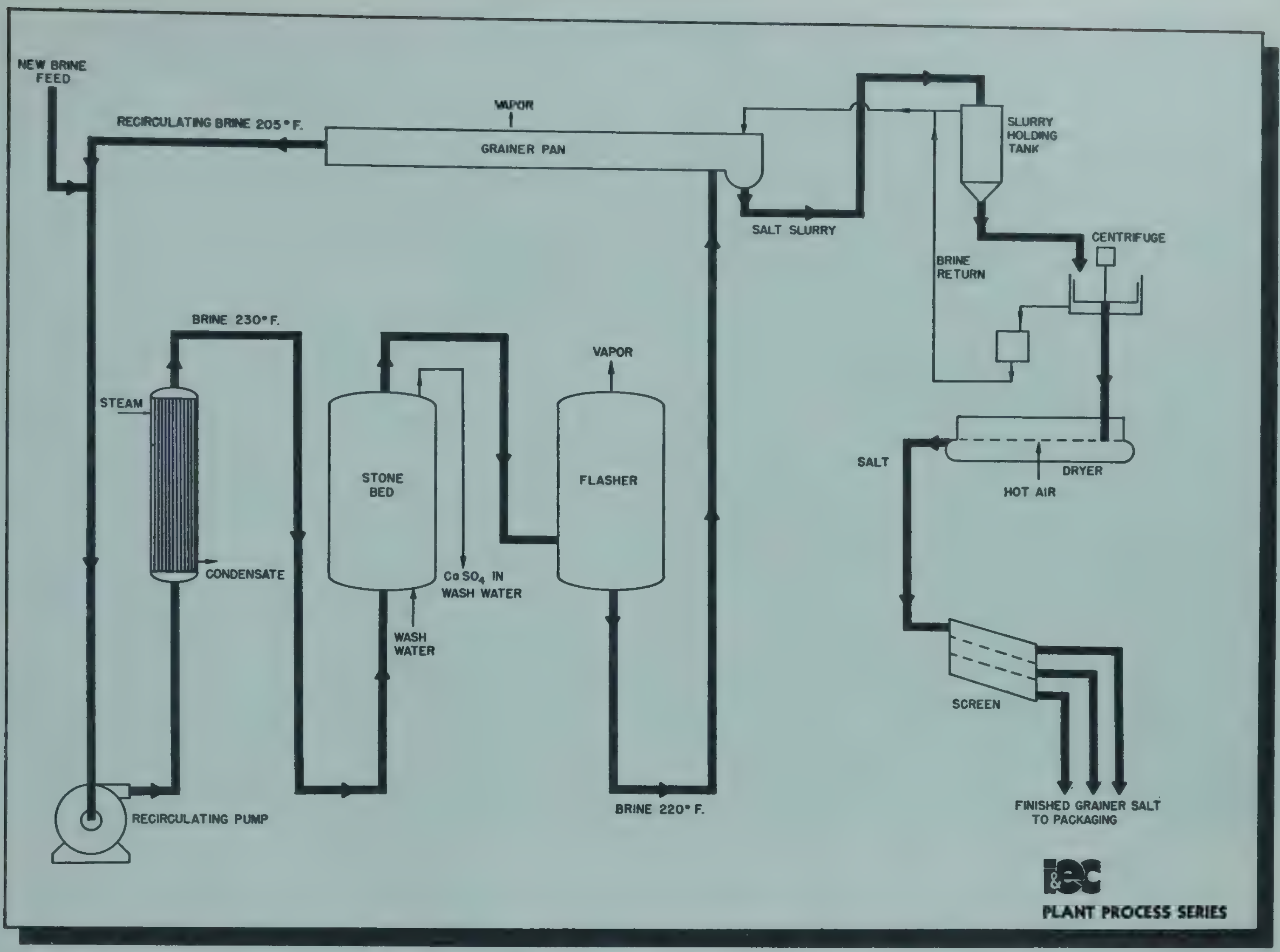


Figure 5. Flow sheet for grainer salt production

to keep salt free-flowing are to pack it in moisture vaporproof containers, or to add a filler to it. An asphalt film having a weight of 25 pounds per 1000 square feet is the usual moisture vapor barrier used. The fillers currently used are magnesium carbonate, hydrated calcium silicate, and tricalcium phosphate, and are added in amounts of 0.5 to 2% depending upon conditions of use. Each of these fillers has the ability to absorb from the salt moisture acquired from the atmosphere and to release this moisture at low humidities. These fillers also have the properties necessary to keep the salt from caking under changing moisture conditions. These fillers must adhere to the salt crystals to form a coat for each crystal and must not become dusty. If it is only necessary to keep the salt from caking this can be accomplished by mixing the salt with either stearates or humectants, such as calcium chloride or glycols. These preventive measures, together with common sense methods of storage, significantly reduced the problem of keeping salt in proper condition for use.

After blending, table salt is packed by automatic packaging machines. Salt is usually shipped commercially in 100-pound multiwall bags. Also a substantial quantity of salt is pressed into blocks of 50 pounds and other sizes. In this operation pressure exerted upon salt in a mold is sufficient to cause the crystals to knit together without the use of an adhesive binder.

Grainer Salt Is Made by Evaporation in Open Pans

The salt produced by the grainer process is a coarse salt having a high rate of solubility in water. This salt is used in the manufacture of cheese and butter. Salt manufacture by this process, however, is several times more expensive than by the vacuum pan method. It takes approximately three times as much coal to make evaporated salt by the grainer process as it does in vacuum pans. Unless the special properties of grainer salt are required for some particular use, the process cannot be justified. At Manistee, production is only a small fraction of the amount made by vacuum pan.

Grainer salt at Manistee is made in four long shallow pans 120 feet long, 16 feet wide, and 2 feet deep. The brine in these pans is maintained at approximately 210° F. by recirculation through external heat exchangers. Each pan will produce 30 tons of salt per day.

The salt is crystallized in the grainer pan as air circulates over the surfaces of the brine. The evaporation, which takes place at the surface, results in the formation of salt crystals which float on the surface of the pan until they grow to sufficient size to sink. These crystals are in the shape of hollow pyramids. The crystal as it starts to form at the surface of the liquid is a cube. The beginning crystal is supported by surface tension in a manner that, except for the top face of the cube, the entire crystal is under the surface of the liquid. Since evaporation occurs only at the liquid surface, the crystal grows—after it reaches a certain size—most rapidly along its top edge. The supporting surface is increased along with the weight, so the crystal sinks a trifle but is still supported. A pyramidal or "hopper-shaped" crystal is thus formed. Because all the brine in the pan is supersaturated, growth of the crystals continues after settling to the bottom of the pan. Calculations show that approximately one half of the crystal growth occurs while the crystals are on the bottom of the pan.

Divided vibrating conveyor carries various size fractions of salt from screen to bins

The equipment used in the production of grainer salt at Manistee, in addition to the pans, consists of a brine circulating pump, a heat exchanger, a stone bed, and a flasher. A flow sheet of the process is shown in Figure 5. The circulating pump maintains a flow of brine through the system at a rate of 1000 to 2000 gallons per minute, depending upon the production required. The brine is heated in the heat exchanger from 205° to 230° F. with steam at 15 pounds per square inch. The function of the stone bed is to remove calcium sulfate from the brine. The brine throughout the grainer system is supersaturated with calcium sulfate and can be removed if there is a surface on which it can precipitate. This stone bed, which consists of a tank 10 feet in diameter and 12 feet high, is filled with 1-inch stones which provide the necessary surface. Calcium sulfate is allowed to accumulate on the stones for a 1-week period and is then removed by washing with water. (Brine temperature is reduced from 230° to 220° F. by evaporation in the flasher so that the brine discharged from the flasher to enter the pan is slightly supersaturated.)

The salt from the grainer must be handled carefully in order to prevent breakage of the crystals since the object of the grainer process is to produce a coarse salt with a high surface area. The salt can be pumped as a slurry with certain types of pumps (*6E, 16E*) with very little breakage. It is dewatered in a batch type centrifuge (*1E*) with the brine being returned to the grainer pans and dried on a deck type dryer (*8E*) in which the salt passes over an electrically vibrated, perforated plate through which hot air is introduced. The salt from the dryer is conveyed to screens with drag conveyors (*12E*). Both the dryer and conveyors are of a type which result in minimum breakage.

Salt is next screened (*15E*) into four different grades depending upon crystal size. The finest grade is extra fine flake salt which will pass a 65-mesh screen, and the coarsest an extra coarse flake salt which is −6 to +28 mesh. Almost all of this salt is packed in 100-pound multiwall paper bags.

Salt Consumption Will Continue to Rise

Salt production in the United States has shown an upward trend for many years and there is every reason to assume that it will continue in that direction. The average person consumes 10 to 15 grams of salt per day, so per capita consumption of salt for food purposes will remain constant but the total will rise parallel with the population curve. The trend toward more factory-processed foods should not affect per capita salt consumption in foods.

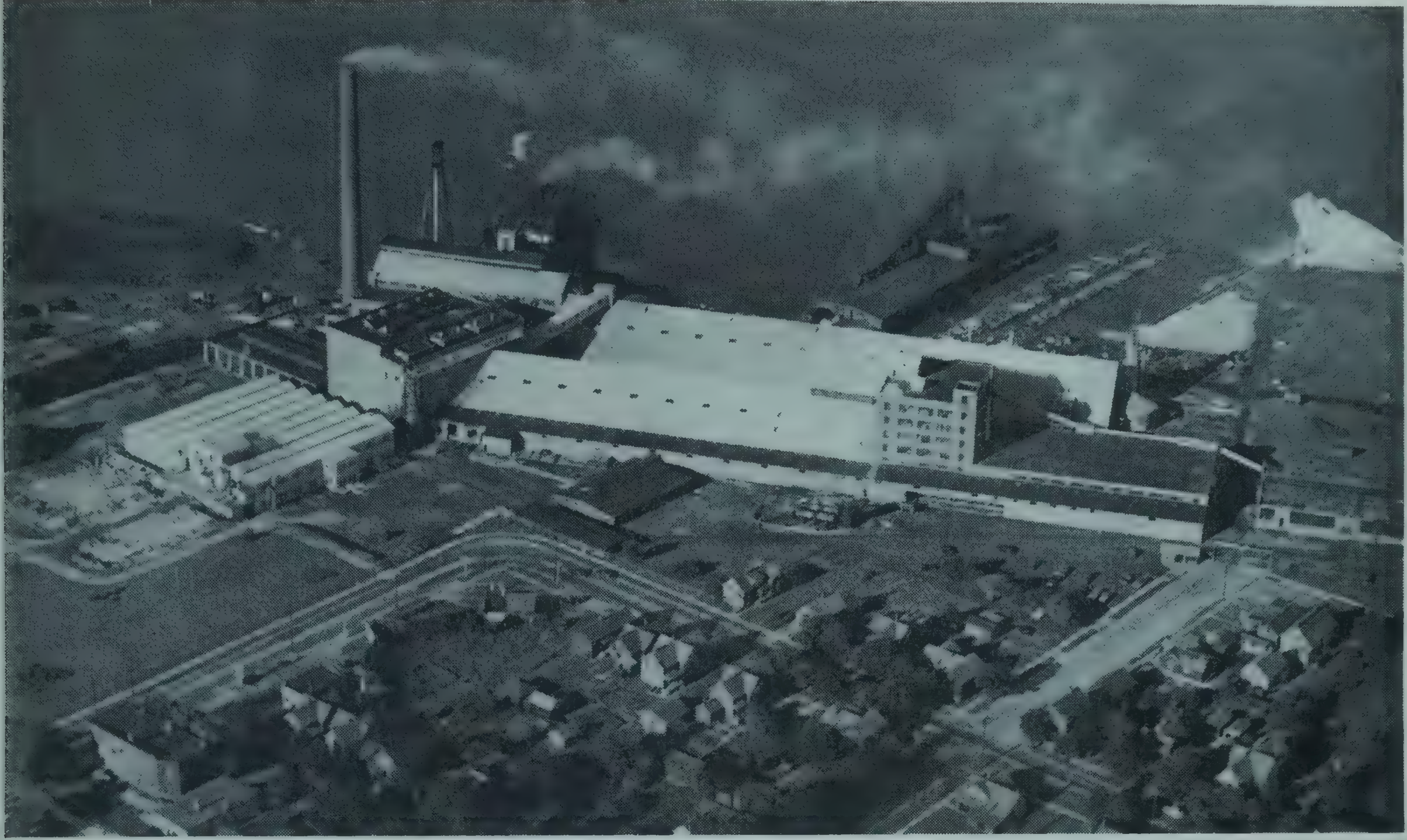
New refrigeration and food preservation techniques in the food processing industries have brought some decreases in use of certain kinds of salt. For example, the railroads use less salt now for icing refrigerator cars because of more rapid car movement. Similarly, the once sizable market for salt for ice cream freezers has dwindled to almost nothing, but the rapid growth in the use of salt for removing ice and snow from highways has more than offset the loss of business due to these changes. Salt is essential in making cheese, butter, other dairy products, baked goods, pickles, and many other foods; special products for these various foods will continue to find substantial markets.

Livestock feeding, a large user of salt, should continue to increase as the feeders become educated to the value of using more salt.

The increasing demand for purer water for municipalities and industries makes the outlook for salt sales for regenerating water softening ion exchange resins one of the most promising of the industrial markets.

By far the greatest growth in salt use has been in chemical manufacturing, which uses approximately 68% of the entire output. Caustic-chlorine facilities are the largest outlets, but salt enters directly or indirectly into almost every phase of chemical manufacturing. Although many chemical makers, such as soda ash, and many caustic-chlorine manufacturers use brine from their own wells rather than salt, about one third of the salt output is sold to chemical manufacturers.

Salt is loaded into ship



Over-all view of Morton Salt Plant at Manistee, Mich.

With many diverse applications in the chemical industry not all changes increase the use of salt. For example, the trend toward synthetic detergents, which need less salt in their manufacture than do soaps, reduces the demand. On the other hand, newer industries like synthetic rubber and metallic sodium open large new markets. Metallic sodium is finding increased application in various organic syntheses and in the metallurgy of some of the new "wonder metals."

Growth of the already gigantic salt industry in recent years cannot compare with the mushrooming of many other branches of the chemical industry, but the increase has been steady and can be expected to continue. The economics of salt manufacture call for large plants. The big investments in existing plants and the fact that unit operations used in the salt industry are among those which have been investigated for the longest time make overnight process changes unlikely. This does not indicate that the industry is static by any means. Morton carries on a continuous program for improvement in operating procedures, and for adapting new equipment and materials of construction for use in its plants. In addition the company recently built a new research laboratory at Woodstock, Ill., in conjunction with its affiliate company, Ringwood Chemical Co., to house an expanding research staff working to improve present products and study possible new ones.

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(17) U. S. Bur. Mines, Washington 25, D. C., **MMS. 2244,** 1953.

Processing Equipment

(1E) American Tool and Machine Co., Boston, Mass., centrifuge.
(2E) Buffalo Wire Works, Buffalo, N. Y., screens for granulated salt.
(3E) Cleaver Brooks Co., Milwaukee, Wis., propellors for evaporators.
(4E) Gump, B. F., Co., Chicago, Ill., gravimetric feeders.
(5E) Link Belt Co., Chicago, Ill., mixing screw conveyors.
(6E) Manistee Iron Works, Manistee, Mich., evaporator bodies and slurry pumps.
(7E) Melchior, W. A., Chicago, Ill., mixing screw conveyors.
(8E) Morton Salt Co., Rittman, Ohio, special deck-type dryer.
(9E) Oliver-United Filter Co., Inc., Chicago, Ill., top feed rotary vacuum filter.
(10E) Omega Machine Co., Providence, R. I., gravimetric feeders.
(11E) Robison, C. S., and Assoc., Chicago, Ill., rotary vacuum filter.
(12E) Stephens-Adamson Mfg. Co., Chicago, Ill., conveyors.
(13E) Sudlow-Saylor Wire Cloth Co., St. Louis, Mo., screens for granulated salt.
(14E) Swenson Division, Whiting Corp., Harvey, Ill., rotary vacuum filter.
(15E) Tyler, W. S. Co., Cleveland, Ohio, screens for granulated and grainer salt.
(16E) Worthington Pump and Machinery Corp., Chicago, Ill., slurry pumps, and propellors for evaporators.

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Vegetable Oil Refining

Demonstration and research refinery integrates existing process techniques to satisfy customer requirements, and extends those principles in the direction of increased savings and improved quality

KEVIN J. BRADLEY, Assistant Editor *in collaboration with*
FRED H. SMITH, The Sharples Corp., Philadelphia, Pa.

ROCK-BOTTOM refining costs based on highest technical efficiency, backed by shrewd business operations in a highly complex commodity market are the ingredients of success, even survival, in the severely competitive billion dollar vegetable oil refining industry. After centuries of traditional operation, 40 years of the application of chemistry and chemical engineering are rapidly approaching the point of recovery down to the last drop from crude vegetable oil.

Vegetable oil refining is carried out in almost every country in the world. Many processes are used, from the age-old simple treatment with caustic to the most modern refineries, complete with high speed centrifuges and complex chemical treatments. In the United States, refining technology is extremely advanced, and increased costs make it imperative that refining be a continuous process and losses be kept to a minimum. Refining loss is a frontier that the industry has been steadily pushing back since 1916, when it was discovered that oil could be recovered from the soapstock formed when caustic neutralized the free fatty acids in the crude oil. Raw vegetable oils usually contain triglycerides of long chain fatty acids, free fatty acids, gummy phosphatides, and color bodies. For use as edible oils, in the production of oleomargarine, shortening, salad oil, and frying oil, fatty acids, phosphatides, color bodies, and other contaminants must be removed. Therein lies the refiner's job. Light oils are used for industrial and household shortenings; darker grades are used in salad oils and yellow oleomargarine, where color requirements may not be so severe. Four to five billion pounds of edible oils are produced annually in the United States. Cottonseed, peanut, soybean, and corn oils are refined in this country; other areas produce palm oil, babassu oil, sesame oil, and many others. Linseed and fish oils are also refined, but are not usually regarded as edible. They find application with other oxidizing oils in paints, printing inks, and so forth.

Many other vegetable oils can be produced, if a market could be found for them that would justify often relatively high costs. Orange and rice bran oils are made from by-products of food processing industries.

Soapstock, the precipitated impurities which are removed from the raw oil, is a real problem to vegetable oil refineries. In a business where costs are figured so closely, storage space and disposal problems for waste products can spell disaster. Most refiners are satisfied if they can dispose of their soapstock and come out even. Soap manufacture is one outlet for soapstock. In some cases, salable fatty acids can be distilled from the acidulated soapstock and used in linoleum bases, cattle feeds, and glyptal resins.

The objective of the vegetable oil refining process is to remove the contaminants in crude oil to produce a neutral oil. Since the most important end uses are in edible products, the refined oil must be fit for human consumption. In general, refining separates the moisture mechanically, precipitates and removes the gums, neutralizes the free fatty acids, and removes the resulting precipitated soap. In all cases it is necessary to reduce color to a point at which it is acceptable to the consumer.

Refining progress is in cutting losses

The story of progress in the vegetable oil refining industry is almost exclusively a story of reducing the amount of salable oil lost during the process. This battle has gone forward on three fronts—removing entrained oil from the soapstock, reducing saponification of triglycerides, and controlling emulsions.

The old kettle refining technique, used from the beginning, consists of adding caustic soda to agitated raw oil in a large kettle holding from 20,000 to 120,000 pounds. The chemistry involved in this simple operation is rather complicated. The natural moisture content of the oils is increased by the amount of water in the caustic; the added moisture precipitates the gums by hydration. Caustic immediately neutralizes the free fatty acids, producing a soap relatively insoluble in the oil. The amount of caustic used always exceeds the amount necessary to neutralize the acids; the excess is available for treatment of the color bodies.

After a period which may vary from 10 minutes to more than 1 hour, agitation is slowed and temperature is raised to obtain a "break." The precipitates are allowed to settle, and are drawn off through the bottom of the kettle. In some countries outside the United States, water is then sprayed on the oil surface and allowed to settle. This washes dissolved and unsettled soap from the refined oil. After several such washings, the oil is vacuum dried in a batch tank.

This process was strictly an art, dependent on an experienced refiner who tasted oils, rubbed soapstock in his hands, and blamed the crude mill for a poor extraction. The usual kettle refiner has at his command caustic soda treats, time, and temperature. His soapstock waste, however, will contain up to 30% neutral oil and significant quantities of soap produced by saponification of edible triglycerides.

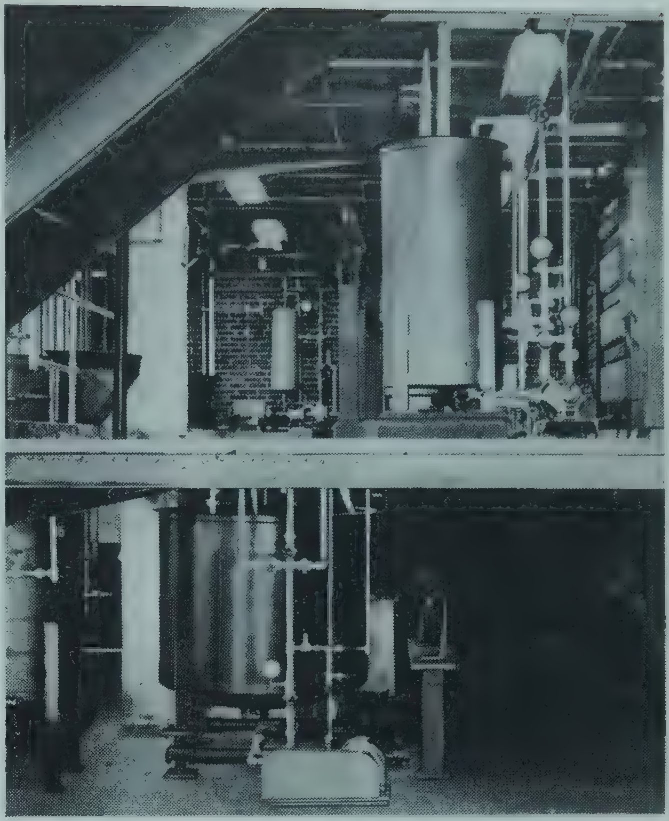
In 1916 it was discovered that some of this lost oil could be recovered by proper application of process chemicals and machines. The soapstock was diluted with water until it went into solution, and an oily emulsion was separated from the soap and water solution in a centrifuge. This emulsion could be broken with salt, and a low grade clear oil was separated from the aqueous phase by means of a second centrifuge. Thus, by reducing the electrolyte concentration of the water phase the soap would go into solution, and the separated emulsion could be made to give up a portion of its entrained neutral oil by breaking it with salt. About 60% of the entrained neutral oil in kettle soapstock is recoverable by this process.

In the years after the first World War, a rise in black grease price reduced the margin for this operation; dozens of plants were idle for about 10 years. The lessons taught by this process, however, showed the possibilities in centrifuging the whole oil rather than only the soapstock. At least two independent groups started working in that direction, The Sharples Corporation and Refining Unincorporated.

From the first few years' work emerged the continuous centrifugal refining process, which added centrifugal force to the factors available to the refiner. Sharples installed its first vegetable oil refinery in 1932 and since that time has set up 175 plants around the world, with a combined capacity in excess of 400 tank cars (24,000,000 pounds) of refined oil per day. Introduced in 1932, continuous centrifugal processing had as its fundamental advantage the substitution of centrifugal force for gravity in settling out the contaminants, and very short contact times. Forces exceeding gravity by at least 13,000 times are capable of compressing the soapstock in such a way that less usable and salable oil is lost during the separation. Refining is accomplished very quickly; excess caustic is not in contact with neutral oils long enough to hydrolyze them and cause additional losses. Fundamental process chemistry is the same as that employed by the kettle refiner, but during the thirties caustic centrifugal refining was capable of returning profits to the refiner which could pay off its capital costs in one year or less.

By reducing contact time between caustic and crude oil from a matter of hours to a few minutes, continuous refining considerably reduced saponification of edible triglyceride as a source of loss. In many cases saponification can cause losses up to 1% of the total crude oil. Process flexibility was also an advantage of continuous refining. Since soapstock is separated in a centrifuge, a clean break is not necessary, and a wide range of caustic treats and strengths is possible. Equipment required for continuous caustic centrifugal refining includes a scale tank for weighing crude oil, a proportioner for adding measured amounts of reagents, mixers, heaters, and centrifuges. The oil is also treated once or twice with water and separated to wash out residual soap. Continuous vacuum drying is used to remove the last traces of water.

At this point it is desirable to jump almost a quarter of a century. In December 1954, Sharples officially announced its demonstration and research refinery. Pilot-scale research is no longer worth while in this extremely competitive industry; economies possible through full scale production are the technical factors which determine success or failure in vegetable oil refining. Process evaluations must be carried out on a fully commercial scale, although none of the refined oil will be for sale, to determine the exact economics of the application of the various refining methods to raw vegetable oils.



Lower two floors of three-floor Sharples Vegetable Oil Research and Demonstration Refinery

Lower level, oil storage tanks; upper, reagent tanks, with scales under all tanks

In carrying out work for customers, Sharples encourages the customer's engineers to come and see their problem worked through. Any of the major processes used in vegetable oil refining can be carried out in this plant, which has a capacity of 60,000 pounds per day. It occupies more than 9000 square feet, on three floors, and its heart is the system of weigh tanks. Placed throughout the refining system, they permit accurate recording of every crude oil constituent or reagent going into the process or removed as a by-product or a waste. In this way, accurate comparisons of processes and of variations in processes are possible; results can be compared and reproduced with similar equipment anywhere in the world. New equipment which might bring further economies to the refining process is also evaluated and improvements made, such as a new ratiometer (*6*, *16E*).

The refinery is designed so that various pieces of equipment may be used or bypassed as the needs of the specific problem dictate. This is clearly shown on the flow chart (Figure 1), which follows the process described above through the demonstration refinery, and shows the variations in equipment used when refining is done by two major processes which will be described later. Detailed discussion of large-scale operation of some of these processes, together with some historical background and literature references, has been given in a previous report in this staff-industry series (*5*). For a clearer understanding of the philosophy behind the demonstration refinery—why it was built and what it can do—it seems desirable, however, to interject a brief discussion of the individual major processes from the standpoint of their chemistry and their distinctly different approaches to the solution of some of the problems which have been encountered in vegetable oil refining, following them generally through the refinery by the flow sheets and by the oil refining variation

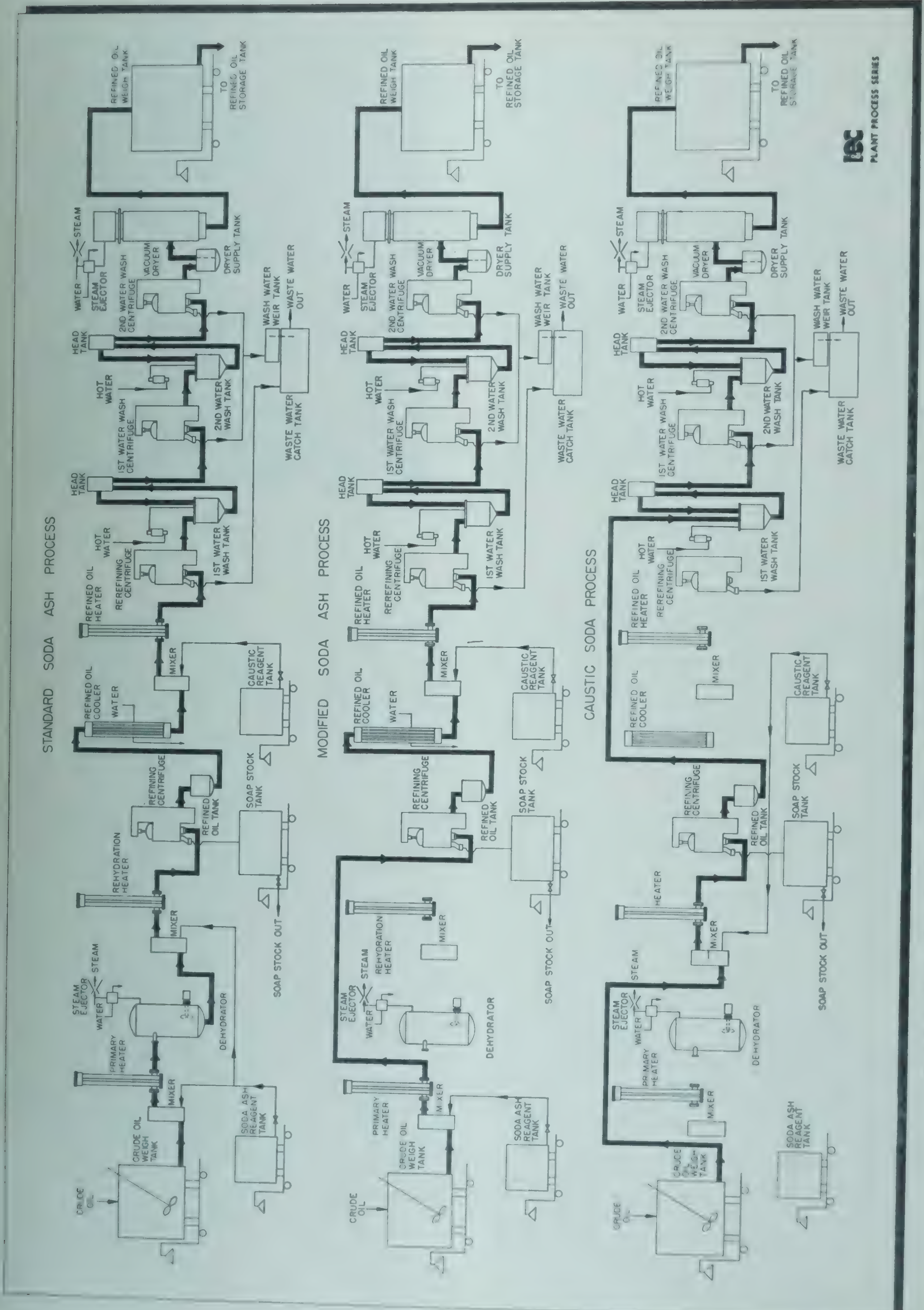

STANDARD SODA ASH PROCESS
MODIFIED SODA ASH PROCESS
CAUSTIC SODA PROCESS
CRUDE OIL
CRUDE OIL WEIGH TANK
MIXER
PRIMARY HEATER
SODA ASH REAGENT TANK
STEAM EJECTOR
WATER
STEAM
DEHYDRATOR
REHYDRATION HEATER
HEATER
SOAP STOCK OUT
SOAP STOCK TANK
REFINING CENTRIFUGE
REFINED OIL TANK
REFINED OIL COOLER
CAUSTIC REAGENT TANK
REFINED OIL HEATER
REREFINING CENTRIFUGE
HOT WATER
1ST WATER WASH TANK
HEAD TANK
1ST WATER WASH CENTRIFUGE
2ND WATER WASH TANK
WASTE WATER CATCH TANK
WASH WATER WEIR TANK
WASTE WATER OUT
2ND WATER WASH CENTRIFUGE
VACUUM DRYER
DRYER SUPPLY TANK
REFINED OIL WEIGH TANK
TO REFINED OIL STORAGE TANK
I&EC PLANT PROCESS SERIES

Figure 1. Flow sheet of three processes in The Sharples Corp. demonstration and research vegetable oil refinery

Table I. Vegetable Oil Refining Variation Chart

(X denotes equipment used in each process)

Refining step	Equipment used	Process Methods: Caustic	Soda ash	Modified caustic	Ammonia	Modified soda ash	Services	Waste Streams Out
Crude oil ↓								
Weigh	Scale	X	X	X	X	X		
Primary refining	Ratiometer		X	X				
			+ Na_2CO_3	+ Na_2CO_3				
	Mixing zone		X	X				
	Heater		X				Steam	
	Dehydrator		X				Steam water	Water
	Ratiometer	X	X		X	X		
		+ NaOH	+ Na_2CO_3		+ NH_4OH	+ NaOH		
	Mixer	X	X		X	X		
	Heater	X	X	X	X	X	Steam	
	Centrifuge	X	X	X	X	X		Soapstock + H_2SO_4 → mineral acid sewage
						+ Na_2SO_4		
Color rerefining	Cooler		X	X	X	X	Water	
	Ratiometer		X	X	X	X		
			+ NaOH	+ NaOH	+ NaOH	+ NaOH		
	Mixer		X	X	X	X		
	Heater		X	X	X	X	Steam	
	Centrifuge		X	X	X	X		Rerefining lye
			+ water	+ water	+ water	+ water		
First water wash	Mixer & heater	X	X	X	X	X	Steam	
	Centrifuge	X	X	X	X	X		Wash water
Second water wash	Mixer & heater	X	X	X	X	X	Steam	
	Centrifuge	X	X	X	X	X		Wash water
Vacuum dry	Vacuum dryer	X	X	X	X	X	Steam water	Water
Weigh	↓ Scale	X	X	X	X	X		
Refined oil								

chart (Table I). This table complements the flow sheet in summarizing the reagents, services, and waste streams involved in all the major processes. In addition, materials balances in the demonstration refinery for two processes will be given, and palm oil refining will be followed in complete detail through the refinery.

Saponification losses can be eliminated

During World War II Refining Unincorporated sought to increase centrifugal refining profits by developing a process using a nonsaponifying reagent which would neutralize the free fatty acids and properly hydrate the phosphatides. When refining with caustic, a soap phase is produced in which both oil and caustic are soluble. This intimate contact results in saponification, a process difficult in the absence of soap. When caustic is added to a kettle of fat in soap manufacture, saponification goes very slowly at first. This is because there is no soap present in the kettle to catalyze the reaction; as soon as a small amount of soap is present the saponification proceeds rapidly.

The soda ash process, offered for sale in 1945, involves application of sodium carbonate to the oil as a nonsaponifying reagent, followed by dehydration of the mass to remove carbon dioxide and to break emulsions produced between carbonate, water, carbon dioxide, and oil. Soda ash is concentrated to a very high degree in the vacuum dehydration step and successfully breaks any emulsions which might have been formed. The soap produced in this process is not separable in a centrifuge; it is necessary to add a second reagent high enough in electrolyte to maintain a grain in the soap and with sufficient water content to produce a plastic, flowable mass. In general, the first treat is about twice the quantity of soda ash required to neutralize the free fatty acids. The water from this treat is withdrawn from the mass by the vacuum dehydrator. The second treat, sometimes called rehydration, varies from 3 to 7% of 20° Bé. soda ash, in order to produce the grained, plastic soap. The material is then centrifuged at temperatures up to 200° F.

A disadvantage of processes using nonsaponifying reagents is that these chemicals will not remove color. An additional step using caustic must be inserted, but since the purified oil now contains no soaps, reaction between caustic and triglycerides is very slow and losses through saponification are relatively small. This rerefining step is similar to the primary refining of the original caustic process. Excellent colors can be obtained.

The soda ash process has been accepted fairly widely in the United States, although the high capital investment required has discouraged its use in foreign countries. Only one plant has been built for the process outside of the United States and Canada. High initial outlay is required for triple proportioning and the dehydrator and its associated vaporizing heater.

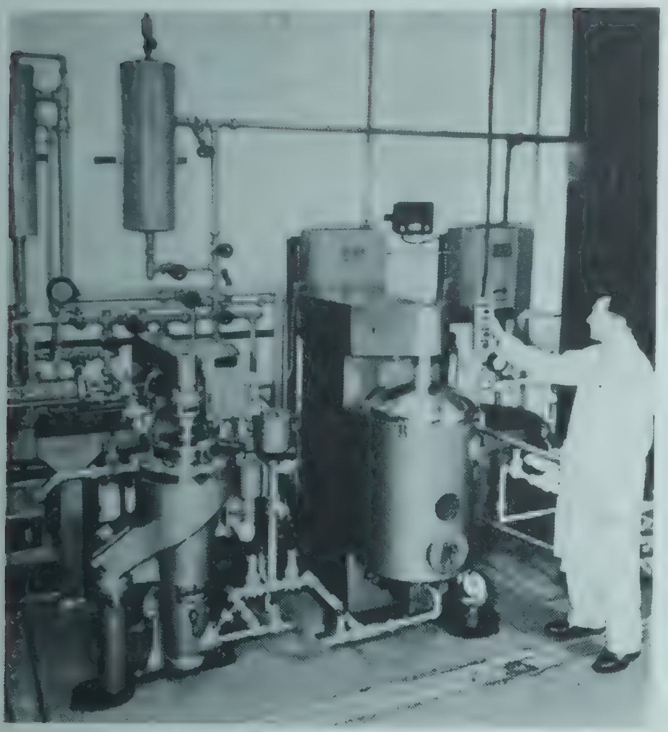
Another difficulty is the large quantity of soda ash used in refining, which appears in the soapstock. Sulfuric acid acidulation must be used to spring the sodium soaps into salable black grease, since soda ash soapstock is too low in fatty acid content to be marketable. Large quantities of acid waste are a real problem. Most cities will not allow this volume of effluent to be introduced into the municipal sewer system. Otherwise, however, the savings possible make the process economically attractive. Many companies adopted the process immediately, in view of financial returns possible.

Soap characteristics are important

In 1950, another process appeared which has found considerable acceptance abroad. Saponification is controlled by use of exactly the amount of caustic calculated to be a stoichiometric treat for the free fatty acids in the crude oil. The smaller the soap volume (soapstock plus water) is, the less neutral oil is entrained; for this reason, high Baumé caustic is used. In general it runs no less than 26° Bé.

A treat of this kind produces a soap which fluctuates in texture as the crude oil changes. Since stable conditions are always the criterion of maximum efficiency within a separating centrifuge, a flush reagent (usually sodium sulfate) can be introduced into the bowl in such a way that it will act as a stabilizing carrier liquid for the soapstock but will not contact the oil at any time.

By this means crude oils can be chemically treated so that the best separation can be obtained within the centrifuge and also in such a way that saponification is minimized when using caustic. The process is still flexible enough to produce a soap, after it has been separated from the oil, which is the best type of soap for discharging from a centrifuge, for entrainment of neutral oil, and for the absorption of all the water phase which has been separated during the refining step. Under such conditions there is insufficient caustic remaining after neutralization of the free fatty acids to reduce color, and the rerefining step is again necessary. Here again, lack of phosphatides or soap in the oil after



Operator starts centrifuge used for primary refining of vegetable oil

primary refining holds down saponification losses; excellent colors are available without damage to savings.

Processes of this type have been installed in almost every foreign country outside Canada and the United States, with variations which include primary degumming before refining, double rerefining in one or two cases, and without flexibility of the flush reagent in some plants. By adding citric acid to the crude oil, the amount of neutral oil dissolved in the gums is reduced, making more oil available for recovery. Since 1950, about 40 plants using this modified caustic process have been installed.

Another nonsaponifying reagent which can be used in vegetable oil refining is ammonia. Several years ago, Refining Unincorporated introduced a process using aqueous ammonia as the primary refining agent. Ammonia is metered into the raw oil in much the same way as caustic or soda ash would be; however, in this case, the reaction between ammonia and the free fatty acids, releases no secondary gas. Thus, the additional equipment necessary with the soda ash process is not necessary with the ammonia process. It is similar to the modified caustic process as far as equipment is concerned, although in this case very high Baumé ammonia strengths are not possible, nor is it necessary to cut down the total water phase in order to reduce emulsions. A flush system is not needed on primary refining.

Capital outlay is somewhat increased, because all equipment must be totally enclosed, including reagent tanks, water wash tanks, and all soapstock containers. Although ammonia is not considered a hazard, it must be carefully controlled. This process might not appear attractive at first glance because of difficulties in handling the reagent and because the savings are not significantly greater than other process possibilities of equal or less capital investment. However, ammonia can be eliminated from the soapstock simply by heating, reconverting the phosphatides and fatty acids to the condition in which they exist in the crude oil. Since water soluble gums are not removed with a mineral acid phase, as in normal acidulation, this material is not salable for fatty acid distillation. It does have a potential use for pelletizing cattle feeds. The ammonia can be recovered and reused.

Although there are no plants in actual operation using the ammonia process, several plants have experimented with it sufficiently to state that it is satisfactory from an operating point and that it can be installed without difficulty. A big advantage is lack of undesirable effluents that create a sewage problem.

Modified soda ash process is most satisfactory

Although the soda ash process has many advantages, its high capital investment plus the use of excessive quantities of sulfuric acid are important drawbacks. Without these disadvantages it would be the obvious process for most refiners to use. Considerable work has been done along these lines, and the "modified soda ash process" is now considered by many to be the most economical and the most satisfactory process for the refining of any of the oils processed in the U. S.

In 1954, a system was introduced which was widely accepted among soda ash refiners. A large excess of sodium carbonate, approximately equal to the total amount of sodium carbonate used in the original carbonate process, is introduced into the oil and no dehydration is applied to the mass.

Capital investment is reduced by elimination of the dehydrator and heater, unnecessary if careful control is maintained over the addition of sodium carbonate in primary refining. The troublesome carbon dioxide released when soda ash neutralizes the free fatty acids of a crude oil is kept under control by providing sufficient excess reagent to chemically combine with the carbon dioxide to make sodium bicarbonate. Under these conditions, neither emulsions nor floating soap cause difficulty in the primary separation stage.

Colors obtained on dark cotton oils have been striking; savings have been in the neighborhood of 30%. This process is so attractive that it was adopted by most of the soda ash refiners within the first two or three months of its introduction, with no investment in new equipment. Cottonseed oil from Egyptian long staple cotton, now grown in West Texas and Mexico, produces an oil of exceptionally dense color. The modified soda ash process has been used successfully even on this oil.

The modified soda ash process has been improved since its introduction; it is now possible to treat the crude oil with soda ash in an amount no greater than that required for primary neutralization alone in the original soda ash process, and then centrifuge the oil with no difficulty. In certain instances this has been done by the use of a hermetic machine controlling the carbon dioxide by solubilizing it under pressure; in other cases a small vent tank has been added to eliminate this gas. At no time has the gas turned out to be a difficult problem. The refining reports on actual typical cottonseed oil runs show the distinct improvements both in quality and reduced losses.

The soapstock by-product from this process analyzes above 35% of the total fatty material (soapstock plus entrained neutral oil); can be controlled from 37 to 40% of the total fatty material depending upon the concentration of the original soda ash and the treat which is used. If the treat drops below twice the amount necessary to neutralize the free fatty acid, primary refining is not complete. This lack will result in a lower loss in this primary step. The rerefining step makes up the difference; the result is not far from 30 to 35% savings in either case.

Water white oils can be produced by miscella refining

Color bodies start to oxidize immediately upon being released from the oil seed. With cotton seeds, for instance, the color bodies have tinted the oil beyond recovery within a 0.5 or 1 hour. However, if refining can be carried out immediately, and at relatively low temperatures (high temperatures, about 140° F., "set" the color), oils which bleach to essentially water white color can be obtained with good savings. This is only possible when oil seeds are solvent-extracted, and the refinery must be integrated with the extraction plant. The process is known as miscella refining, and for cottonseed oil must be carried out within 20 to 30 minutes after the oil has been extracted from the seed. Miscella is a mixture of crude oil and extraction solvents, usually hexane. The solvent is removed with stripping steam which both raises the temperature beyond safe color limits and participates in color body oxidation; if refining is accomplished before this step very low color oils can be obtained.

Two miscella refining plants are operating in the United States. The process is not practical except at a solvent extraction mill, and it then becomes attractive only if that mill has enough oil of its own to satisfy the requirements of a continuous refinery. Little advantage has been found for miscella refining soybean oil, because the color is of an entirely different nature.

In other refining processes, emulsification is a real problem. Emulsions can appear suddenly and without warning during the refining process; sodium chloride and/or sodium sulfate are used to break them. Some oils are more prone to emulsify than others; coconut oil must be salted before refining is even started, whereas emulsification is rare with cottonseed or soybean oils. Milo maize oil produced in Mexico develops a gelatinous mass which will not separate in a centrifuge except under the most ideal conditions. Emulsions frequently occur when cold water is added to hot oil, making temperature another factor. Oils which can be readily refined with one process form crippling emulsions with another.

The cup test is the yardstick of the refining industry

The development of vegetable oil refining technology can best be measured in terms of the industry's standard oil test. This test, known as the Cup Test, has been developed by the American Oil Chemists' Society (*1*) and is essentially a laboratory replica of the kettle refining technique. The conditions under which the tests are made in the laboratory are carefully controlled; for this reason the test is valid as the basis for all transactions involving the sale of crude oil. All oil transactions are under the control of the National Soybean Processors' Association (*4*), the National Cottonseed Products Association (*3*), and the AOCS. All of these organizations derive their authority from the producers and refiners themselves.

Rules have been established whereby any oil which is better or worse than industry averages must be sold with standard premium or penalties attached to the basis of sale. For example, a cottonseed oil which demonstrates a cup loss of less than 9% will be billed to the customer at a price which represents ³/₄ of 1% pre-

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Refining Report

Kind of oil: Cotton **Kind of refining:** Modified Soda Ash **Date:** 1/11/55

Analysis of Crude Oil (Sample 35)

FFA 0.75% Cup Loss 5.54% Wesson 2.73%
Color: Refined 5.0/35 Bleached 1.2/10

Analysis of Soapstock (Sample 35-R)

H_2O 28.04% TFA 39.3% N.O. (Dry) 19.9%

Analysis of Oil

	Sample	Soap	FFA	Bl. Color
Refined	35 R	—	0.06%	
Rerefined	35 RR	—	0.02%	
1st wash	35-W-1	176	0.02%	
2nd wash	—	—	—	
Dried oil	35-D	—	0.03%	13/1.3

Analysis of Aqueous Effluents

	Sample	TFA	H_2O
Rerefining	35 RR	4.54%	93.07%
1st wash 2nd wash	35-W-2	0.559%	

Weights

	At start	At end	Net	Treat
Crude oil (5)	3409	7	3402	
Ref. oil (4)	10	3278 samples	3268	
Ref. oil (13)	1845		2	
Reagent (7)	491	428	63	1.85%
Reagent (8)				
Soapstock (9)				
Reagent (10)				
Reagent (11)	457	385	72	2.12%

Per cent: Loss 3.89% Saving 29.7%

Remarks:

Mechanical Hook-up

Dehydrator	No
Gas vent	Yes
Refining mixer	Zone
Rerefining mixer	3 D
Heating before mixing	No
Cooling before reref.	Yes
Setting prop. No. 1	0.86
Setting prop. No. 2	0.86

Ring Dams

As 26 refiner	52
No. 16 refiner	—
As 26 rerefiner	42
No. 16 water wash	29

% Treats (give Bé. & kind)

Neutralization	—
Refining	2% 26° S.A.
Rerefining	2% 26° C.
Refining bowl flush	—
Rerefining bowl flush	20%
1st water wash	15%
2nd water wash	10%
Auxiliary liquid	—

Temperatures

Crude supply (s)	100°
Neutralization	—
Dehydration	—
Refining	200°
Cooled oil	80°
Rerefining	150°
1st water wash	160°
2nd water wash	180°
Dryer supply	180°

Refining Report

Kind of oil: Cotton **Kind of Refining:** Caustic **Date:** 1/11/55

Analysis of Crude Oil (Sample 36)

FFA 0.8% Cup loss 5.76% Wesson 2.62%
Color: Refined 35/5.0 Bleached 13/1.3

Analysis of Soapstock (Sample 36-R)

H_2O 37.8% TFA 39.7% N.O. (Dry) 23.9%

Analysis of Oil

	Sample	Soap	FFA	Bl. Color
Refined	36-R	—	0.03%	
Rerefined				
1st wash	36-W-1	122	0.02%	
2nd wash				
Dried oil	36-D	—	0.04%	17/1.7

Analysis of Aqueous Effluents

	Sample	TFA	H_2O
Refining			
1st wash 2nd wash	36-W-2	0.474%	

Weights

	At start	At end	Net	Treat
Crude oil (5)	3420	8	3412	
Ref. oil (4)	6	3260	3254	
Ref. oil (13)				
Reagent (7)	665	549	116	3.41%
Reagent (8)				
Soapstock (9)				
Reagent (10)				
Reagent (11)				

Per cent: Loss 4.63% Saving 19.6%

Remarks: Soapstock heavy but apparently dry. Required no steam.

Mechanical Hook-up

Dehydrator	—
Gas vent	No
Refining mixer	3-D
Rerefining mixer	—
Heating before mixing	No
Cooling before reref.	—
Setting prop. No. 1	1.58
Setting prop. No. 2	—

Ring Dams

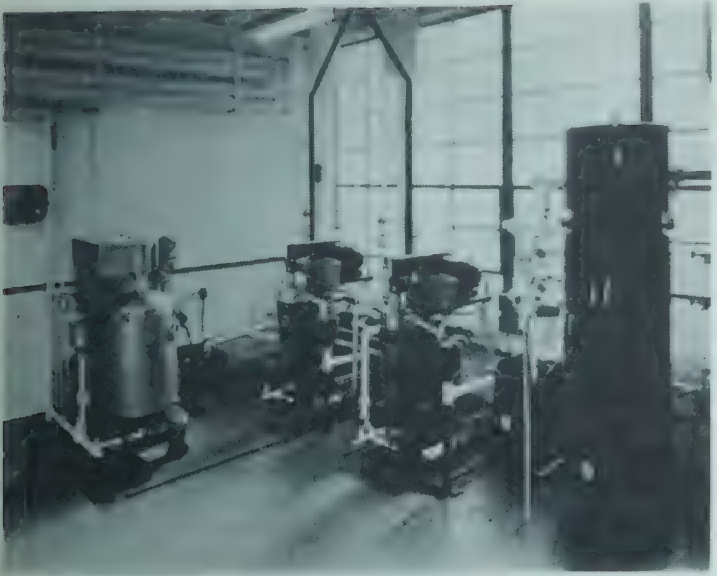
As 26 refiner	46
No. 16 refiner	—
As 26 rerefiner	—
No. 16 water wash	29

% Treats (give Bé. & kind)

Neutralization	—
Refining	3.4% 16° C.
Rerefining	—
Refining bowl flush	—
Rerefining bowl flush	—
1st water wash	15%
2nd water wash	10%
Auxiliary liquid	—

Temperatures

Crude supply (s)	100°
Neutralization	—
Dehydration	—
Refining	140°
Cooled oil	—
Rerefining	—
1st water wash	160°
2nd water wash	180°
Dryer supply	180°



Following rerefining in centrifuge at left to remove color, vegetable oil is washed, centrifuged in two successive stages, and vacuum dried at right

mium for each 1% that the oil analyzes better than 9%. In the same way, there have been established color standards. If, for example, oil has to be sold as a prime summer yellow cottonseed oil it must refine to a color better than 7.6 red on the Lovibond scale. If this is not true the seller must take a penalty of $^1/_2$ of 1% of his basic price for each one point red above 7.6.

The AOCS approves referee chemists throughout the United States whose job it is to analyze samples from every tank car of oil sold on the open commodity market. In case of dispute the decision of these chemists is final. It is even necessary to have the personnel taking the sample of oil certified. In this way all of the transactions are based on a standard quality of oil and profit or loss can be determined ahead of time.

Recognition of these rules is extremely important. As much money can be made or lost by buying and selling oil as can be made in the production itself.

Plant location will largely determine which oils can be handled most efficiently from the economic point of view. The big soybean crops are in the West, sunflower oil comes largely from Canada, cottonseed oil comes from the South and Southwest.

Since oil is bought and sold on basis of refining loss determined by standard cup test, refining methods are judged by their savings against this test. Refining progress can be seen in continual chipping away at the standard refining loss. Average cup test loss for cottonseed oil used to be 9%, meaning that 9% of the crude oil is lost in the cup test. Today, cup loss is usually about 6%, due to changes in crude oils and in extraction methods.

Kettle refining losses are usually in excess of the cup loss since kettle operators find it difficult to consistently meet a carefully controlled laboratory technique. For a 6% oil loss, approximately 3% represents contaminants which must be removed and thus 50% at least of the refining loss is salable neutral oil which might be recovered.

Normal kettle refining produces a soapstock containing at least 30% neutral oil. Application of the centrifuge in continuous caustic refining, plus the integrated process combination of short time and control of caustic treat and strength reduce this figure to about 15% and can save 20 to 25% of the kettle losses. This figure is seldom greater than 20% of the cup losses.

Savings between 30 and 40% of the cup loss, representing 80% of the avoidable losses normally encountered in kettle refining, could be obtained with the soda ash process. These savings are shown in Table II. The modified caustic process offers only 27% savings, but it is considerably less expensive to install. Savings with the ammonia process are also of the order of 27%, and this, plus the high capital investment, has probably slowed its acceptance. Cattle feed applications of ammonia process soapstock have not been completely evaluated yet; if this byproduct turns out to be of value, the ammonia refining process may yet prove attractive.

The modified soda ash process, eliminating the capital expense of the dehydrator and capable of producing excellent colors on dark cotton oils, has shown savings consistently of about 30 to 35%.

Savings for miscella refining cannot be established by a cup loss since a cup measurement is impossible for miscella oil. The only basis for comparison would be through a Wesson loss measurement, difficult to correlate because few such measurements have been made to date on miscella oils. The outstanding advantage of miscella refining is the premium color which can be obtained.

Table II. Benchmarks in Refining Progress

Refining Process	Neutral Oil in Soapstock, %	Savings against Cup Test, %
Kettle	30	Negative
Continuous caustic	20	20
Soda ash	15	35
Modified caustic	15	27
Modified soda ash	15	35
Ammonia	15	27

Soapstock is both a burden and an opportunity

Soapstock problems center on four points: space requirements, cost of reagents and building space, sewage regulations, and maximum income. Many refiners consider themselves fortunate if they are able to dispose of their soapstock at all and come out financially even. Storage space is usually at a premium, refiners cannot often afford disposal costs, sulfuric acid from acidulation cannot be run into sewers as such. However, recent advances are encouraging the refiners to regard soapstock as an opportunity for extra profit rather than a liability.

Continuous palm oil refining is new to the United States

Palm oil is growing fast; its development is being encouraged by West African governments as an indigenous industry. Production in 1954 is estimated at 500 million pounds. Each vegetable oil requires different refining methods to deal with varying kinds and amounts of substances in the crude oil. Since palm oil is a relatively new arrival on the refining scene in this country, its refining technology is not too well known. The crude oil contains from 2 to 8% free fatty acids, almost no phosphatides, and a large amount of miscellaneous dirt introduced by primitive collection methods.

Although the modified soda ash process is the most attractive answer to most refining problems, a special adaptation of the modified caustic process for palm oil has been developed by The Sharples Corp. in Europe and used very successfully in this country. It involves the use of stoichiometric amounts of reagent with sodium sulfate added to raise the electrolyte concentration and prevent emulsions.

Crude palm oil is delivered via tank truck, and is held in a 15,000-gallon steel tank which must be steam heated in cold weather. When the oil is to be refined, it is pumped (*8E*) to an agitated (*6E*) scale tank (*19E*) on the third floor of the refinery, where it is weighed. It is then pumped (*8E*) in a measured (*5E*), regulated (*11E*) stream to a mixer (*15E*), where the free fatty acids are neutralized with a stoichiometric amount of 26° Bé. caustic containing 4% sodium sulfate. The caustic solution is added through a specially designed ratiometer (*16E*). If either a flush system for primary refining or the equipment for rerefining is not available, the treat may be raised to an excess of 0.1% for 1% free fatty acid oils and 0.4% excess for 5% free fatty acid oils. These excesses will aid in producing an emulsion free grain in the primary soap and help reduce color.

The stream is heated to 180° F. in a steam heated heat exchanger (*3E*), equipped with automatic temperature control (*2E*). At the centrifuge (*18E*), a flush of 8° Bé. sodium sulfate, equal to about 6% of the crude oil flow (*10E*), is introduced. The flush helps prevent emulsification; it never touches the oil stream. The soapstock, containing any solid impurities of the crude oil, is expelled and the oil is pumped (*8E*) through a cooler (*4E*).

The principal function of the rerefining step is to reduce color by agglomerating the colloidal color bodies with caustic. In general, palm oil does not require rerefining, since its natural color is quite light. However, where the rerefining step is necessary, a 2% treat of 16° Bé. sodium hydroxide is added through a ratiometer (*16E*), mixed (*15E*), and heated (*3E*) to 160° F. The heat exchanger is steam heated and automatically controlled (*7E*). The mixture of caustic and oil is fed to another centrifuge (*18E*), which removes the agglomerated color bodies.

The refined oil is given two water washings. It is pumped (*22E*) through a mixer and heater combination (*21E*) which maintains a circulation rate three times the flow rate of the process to provide intimate mixing of oil and water. Temperature is automatically controlled (*14E*); water and oil are separated in a centrifuge (*17E*). The water wash is repeated—mixing, heating, and centrifuging—and then the oil is sent to a vacuum dryer (*20E*) equipped with a condenser-ejector (*24E*), where the last traces of water are removed.

The dry, refined oil is pumped (*25E*) to a tank scale (*13E*), where it is weighed. Soapstock, precipitated color bodies, and all other process wastes are also weighed (*12E*), so that a complete materials balance can be calculated.

Instrument air is kept at 30 pounds per square inch. In addition, 100 pounds per square inch air or steam must be available for an occasional blowdown.

Cup tests, free fatty acid determinations, total fatty material determinations, and other analytical operations are performed in a fully equipped laboratory.

Electric power is delivered to a central distribution point (*9E*) at 440 volts and stepped down to 220 volts. All motors are equipped with automatic starters (*23E*). The electric power system is protected by five safety switches (*1E*).

New developments in growing and extracting oils change refining problems

The primary aim of the grower of vegetable oil-bearing crops is a better cash crop per acre. In the last 15 years, changing agricultural techniques have grown more oil on less acreage, introduced new varieties of oil-bearing plants, and changed harvesting methods. An example is the switch to long staple cotton. The farmer's objective is primarily more and better cotton, not more and better oil. Cottonseed oil from long fiber plants is extremely dark in color.

Newer techniques of oil extraction not only extract more oil but also extract worse oil containing more of the undesirable components. Oils extracted by modern methods may contain demulsifiers, reducing the amount of free fatty acid shown in the cup test and the refiner's spread at the same time. Other oil changes are also due to developing technology of extraction (*7*).

Cottonseed soapstock is held in some doubt for animal feed, because it may contain gossypol, a highly poisonous purple pigment present in crude cottonseed oil to the extent of 0.06 to 0.10%. This pigment is completely removable in the refining process. In the cottonseed, gossypol is contained in strong, semirigid gland cells. If these gland walls are ruptured, the pigment is converted to a nontoxic "bound" form (*2*). Heat completely detoxifies gossypol. It can be fed to cattle but not to chickens, because it changes color of eggs to purple.

Soybean oil is rapidly increasing its lead over all other vegetable oils as the world's leader. Peanut oil production is very stable, its unique properties guaranteeing a steady market and a relatively high price. Corn oil is entirely keyed to the production of starch. Linseed oil production is holding its own in spite of the growing popularity of paints based on synthetic materials.

The future of palm oil in the United States is dependent on a reduction in plantation cost and import charges. Plantations are still very primitive in methods of cultivation and harvesting. Although there is no tariff as such on imported palm oil, it must stand a federal "processing tax" of $0.03 per pound. Therefore, the oil must be able to support primitive cultivation and harvesting methods, trans-Atlantic shipping, and the processing tax, and still compete with domestic oils.

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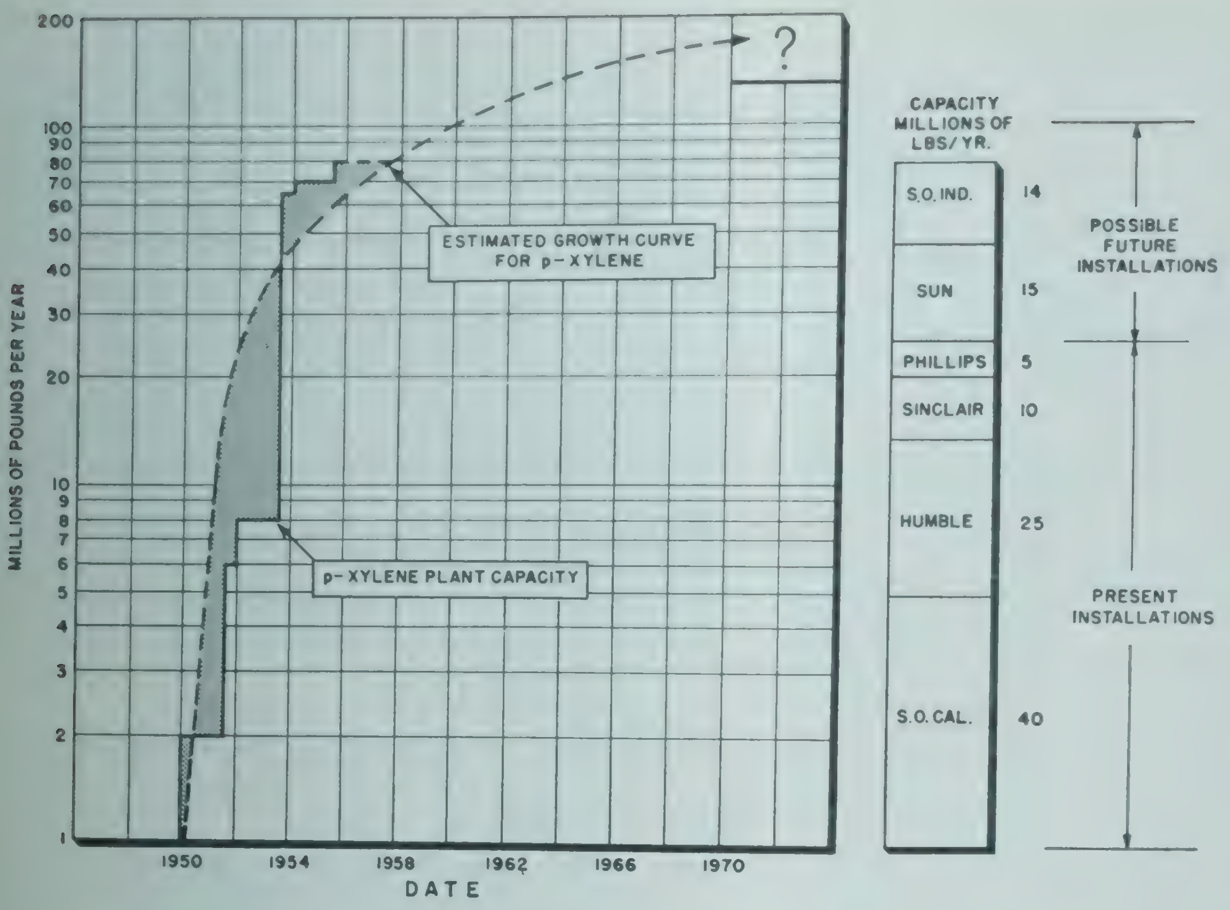


p-Xylene from Petroleum

HARRY W. HAINES, JR., Associate Editor
in collaboration with
J. M. POWERS and R. B. BENNETT
Humble Oil & Refining Co., Baytown, Tex.

COMMERCIAL fractionation of xylenes was launched in the United States during 1945 when Oronite Chemical turned to abundant petroleum-derived stocks for its phthalic anhydride production via the oxidation of *o*-xylene. Meanwhile, another significant development under way simultaneously in England and the United States was soon to create an unprecedented demand for the para isomer.

A polyester fiber had been produced as early as 1931; the first one was described that year at an AMERICAN CHEMICAL SOCIETY meeting by Wallace H. Carothers and Julian W. Hill (*3*, *19*). It had little commercial importance because of its low melting point and poor hydrolytic stability; Carothers then became interested in high molecular weight linear aliphatic polyamides (nylon). His brilliant work, a few years later, caused so much excitement that polyesters were largely neglected. The turning point for polyester fibers came after Carothers' untimely death in 1940, when all of his papers in the high polymer field were collected and published (*24*).

From reading this book, J. R. Whinfield and J. T. Dickson of the Calico Printers' Association in England decided to investigate symmetrical aromatic polyesters. This work, supported by Imperial Chemical Industries, led to the synthesis of polyethylene terephthalate from terephthalic acid and ethylene glycol. It is known in England as Terylene (*10*) and in the United States as Dacron.

Du Pont attempted to produce polyethylene terephthalate during the mid-thirties, but was unsuccessful in its application of nylon manufacturing methods. Word of the British discovery did not reach the United States until the middle of 1944 because of wartime secrecy, and details were not available until early 1945. Du Pont's work on polyester chemistry began in earnest during 1944; company chemists soon synthesized the compound on their own, by procedures nearly identical to those of Whinfield and Dickson. The company now makes three products from this compound: Dacron fiber, Mylar film, and Cronar photographic film base (*5*, *6*, *19*).

The immediate success of polyester fibers caused world-wide production of *p*-xylene, the basic raw material for making terephthalic acid, to increase at a rapid pace. Since 1949, Imperial Chemical Industries has operated a pioneer polymer plant at Huddersfield and a spinning plant at Hillhouse, England. Output from these experimental plants is approximately 2,000,000 pounds per year. Construction on the first large scale Terylene unit as Wilton has been completed and production began in January of this year (*5*, *9*, *16*). When at full capacity, the unit will have an output of 11,000,000 pounds. By the end of the year a second unit of equal capacity will be completed, and by mid-1956 production is expected to reach 22,000,000 pounds. The $56-million plant is manufacturing filament yarn and staple fiber.

Table I. Distribution of C_8 Alkylbenzenes in Products from Catalytic Reforming Processes Per Cent by Volume

		Ethylbenzene		p-Xylene		m-Xylene		o-Xylene	
		Actual	Calcd.	Actual	Calcd.	Actual	Calcd.	Actual	Calcd.
Catalytic Conversion Process	Temp., ° F.	±1.0	±1.5	±1.0	±3.5	±1.0	±5.0	±1.0	±3.5
Hydroforming	925	11.6	10.0	17.1	20.9	46.5	46.4	24.2	22.7
2-Pass fixed bed	850	13.2	9.0	19.1	21.2	48.1	47.3	19.6	22.5
3-Pass fixed bed	875	8.6	9.4	20.3	21.1	52.2	46.9	18.9	22.6
Low temperature fluid bed	800	12.9	8.3	17.4	21.5	45.5	47.8	24.4	22.4
High temperature fluid bed	975	12.6	10.7	19.8	20.6	49.6	45.9	18.0	22.8

A $20-million plant is under construction at Millhaven, Ontario, by Canadian Industries Ltd., to manufacture 11,000,000 pounds per year of Terylene from dimethyl terephthalate (*5*, *6*, *12*, *13*). Hercules Powder will supply dimethyl terephthalate, 12,000,000 pounds per year, from its $4-million Burlington, N. J., plant which is to receive *p*-xylene from Sinclair Chemicals' 10,000,000-pound plant at Marcus Hook, Pa.

Imperial Chemical Industries has world rights for Terylene production, except in the United States. In recent months Imperial Chemical Industries has completed negotiations with a number of European firms, whereby Terylene will be manufactured under license in Italy, France, Western Germany, and the Netherlands (*5*, *9*), but Calico Printers' Association still retains the basic patents and collects royalties.

Terylene's counterpart in the United States, Dacron, has been manufactured by Du Pont under Calico Printers' Association license since 1950. Rapid growth of Dacron has encouraged several petroleum companies into *p*-xylene production and others are actively engaged in planning for future output (*4*, *5*, *7*, *11*, *12*, *13–15*, *27*). The first commercial United States supply of *p*-xylene was manufactured by Oronite Chemical Co. in 1950. Annual capacity in the United States increased from 2,000,000 pounds in that year to an estimated 70,000,000 pounds in 1954, but there has been little improvement in the recovery processes; all companies use low temperature fractionation, although different in operating details from the process pioneered by Standard Oil of California at Richmond, Calif., for production of the material marketed by Oronite.

Domestic p-xylene production may reach 100,000,000 pounds by 1960

Prior to 1940, xylenes were produced mainly from coal tar distillation, but the major portion now comes from petroleum. In 1954, the United States produced 121,000,000 gallons of xylenes (*30*) of which more than 90% was from petroleum conversion processes, as indicated in Figure 1. The synthesis of xylenes is accomplished by catalytic reforming of virgin naphtha stocks containing major concentrations of naphthenic hydrocarbons. Naphthenes are dehydrogenated to yield the corresponding aromatic compounds which may be separated from paraffinic and olefinic compounds in the product by solvent extraction or extractive distillation (*23*). The concentrated xylenes contain the four C_8 aromatic compounds and small amounts of toluene and C_9 aromatics.

Although xylenes are produced by a wide variety of feed stocks and by a number of different catalytic reforming processes, the composition of the product mixture does not vary greatly. This is illustrated in Table I by data (*21*) on different types of catalytic conversion processes which compare analytical results with the distribution of C_8 alkylbenzenes calculated from thermodynamic equilibria. Comparable data from platinum catalyst reforming indicates a similar isomer distribution. The calculated value for *p*-xylene varies from 20.6 to 21.5% for a temperature range of 800° to 975° F., but the determined value is always lower. Equilibrium concentrations of the C_8 alkylbenzenes for the temperature range of 200° to 1600° K. have been calculated by Taylor and others (*20*).

A survey (*25*) made by Ebasco Services, Inc., in 1952, estimated that total U. S. xylenes production would reach 133,000,000 gallons per year by 1953 and would increase to 175,000,000 gallons by 1955. These predictions were obviously somewhat optimistic in the light of recent production figures. Assuming, however, that xylenes capacity will continue to grow at its present rate, total production should be well over 140,000,000 gallons per year by 1956. Assuming further that 10% of the xylenes is recoverable as *p*-xylene, the total amount of *p*-xylene available for chemical raw material use would be approximately 100,000,000 pounds per year, which coincides closely with the present estimated production capacity for 1960. This estimate is based only on the amount from xylenes recovered by fractional crystallization; it does not allow for improved recovery processes in the future that may give higher yields.

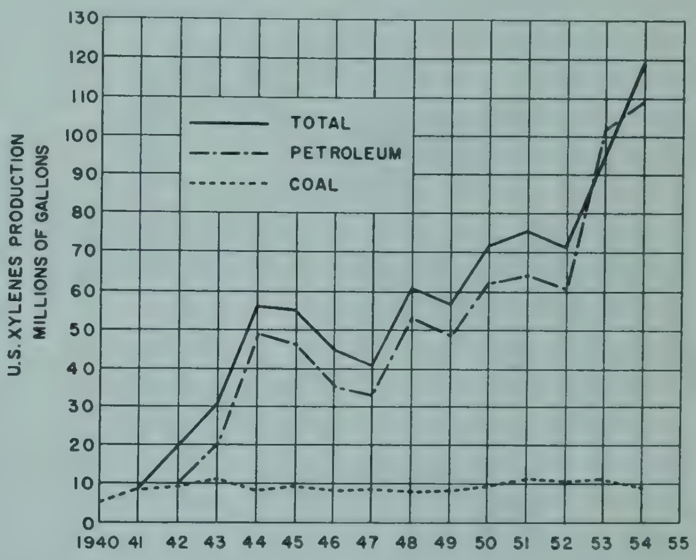


Figure 1. United States xylenes production

Low temperature crystallization is the standard recovery method

The boiling points and freezing points of aromatic compounds generally found in a mixture of commercial xylenes are listed in Table II. With the exception of toluene, the boiling points are very close together. Separation of toluene by distillation may be accomplished readily, and separation of *o*-xylene is done commercially, although with more difficulty. Separation of ethylbenzene or *m*-xylene from *p*-xylene by distillation is highly impractical because of the small difference in their boiling points.

The freezing point of *p*-xylene is a great deal higher than that of its associated isomers and use is made of this physical property for carrying out the separation of *p*-xylene from its mixtures. Although several variations of crystallization procedures are known, fundamentally all utilize the same principle—low temperature chilling and separation of the crystals by mechanical devices. The first known commercial process for separation of *p*-xylene by low temperature crystallization was operated by

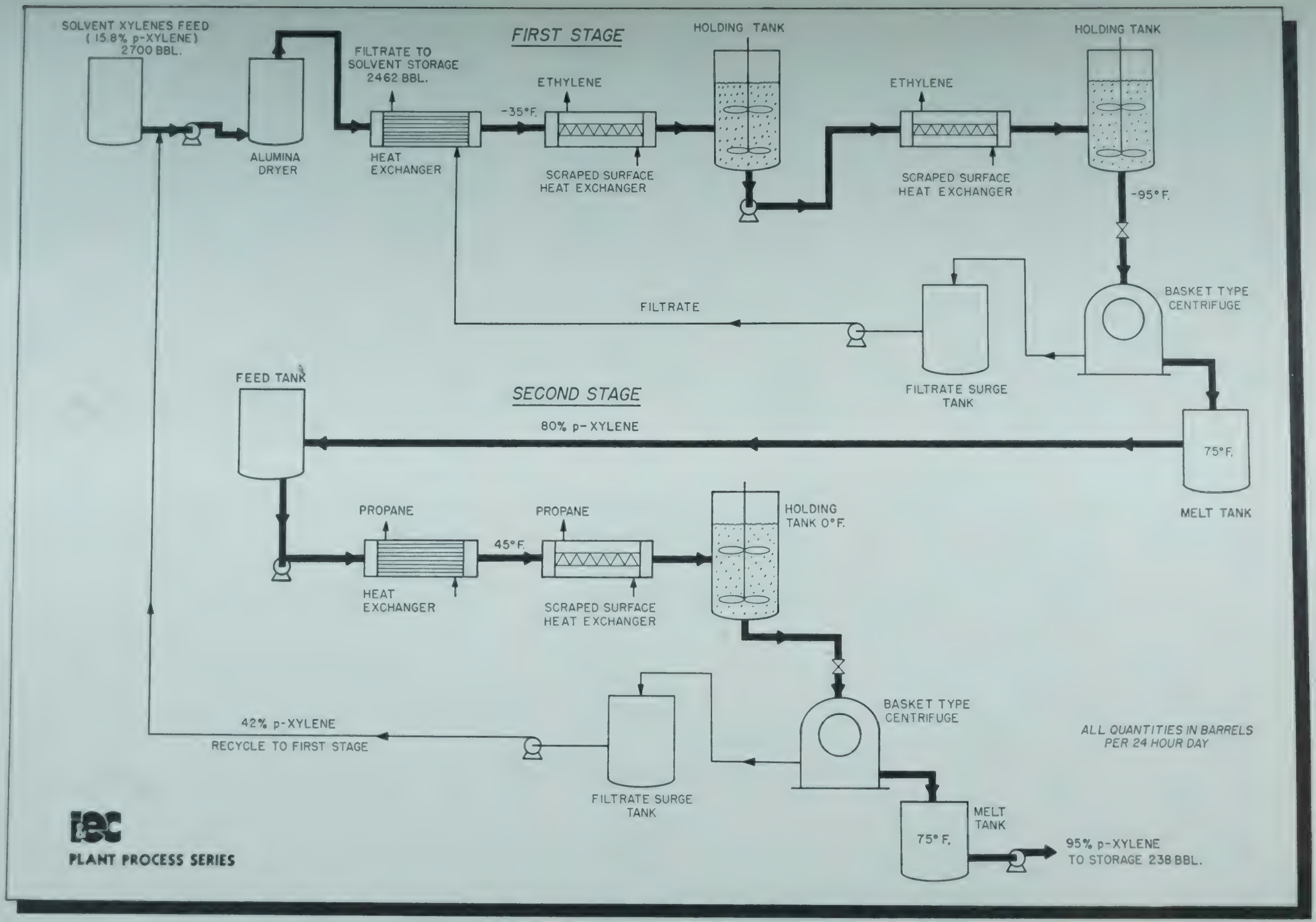

SOLVENT XYLENES FEED
(15.8% p-XYLENE)
2700 BBL.
ALUMINA
DRYER
FILTRATE TO
SOLVENT STORAGE
2462 BBL.
FIRST STAGE
HEAT
EXCHANGER
-35°F.
ETHYLENE
SCRAPED SURFACE
HEAT EXCHANGER
HOLDING TANK
ETHYLENE
SCRAPED SURFACE
HEAT EXCHANGER
HOLDING TANK
-95°F.
BASKET TYPE
CENTRIFUGE
FILTRATE
FILTRATE SURGE
TANK
75°F.
MELT TANK
FEED TANK
SECOND STAGE
80% p-XYLENE
PROPANE
HEAT
EXCHANGER
45°F.
PROPANE
SCRAPED SURFACE
HEAT EXCHANGER
HOLDING
TANK 0°F.
BASKET TYPE
CENTRIFUGE
ALL QUANTITIES IN BARRELS
PER 24 HOUR DAY
42% p-XYLENE
RECYCLE TO FIRST STAGE
FILTRATE SURGE
TANK
75°F.
MELT
TANK
95% p-XYLENE
TO STORAGE 238 BBL.
I&EC
PLANT PROCESS SERIES

Figure 2. Flow sheet for production of *p*-xylene at Humble Oil & Refining Co., Baytown, Tex.

Table II. Boiling Point and Freezing Point of C_7 and C_8 Alkylbenzenes (*1*)

Compound	Boiling Point, ° F.	Freezing Point, ° F.
Toluene	231.12	−138.98
Ethylbenzene	277.13	−138.96
p-Xylene	281.03	55.87
m-Xylene	282.39	− 54.17
o-Xylene	291.94	− 13.33

I. G. Farbenindustrie as early as 1937 (*2*). The method used by I. G. Farbenindustrie, however, was discontinuous and apparently was employed on a small scale; known processes operating in the U. S. are continuous.

Eutectic point limits *p*-xylene yield to 10% of the xylenes

In the initial development work on low temperature crystallization processes, solubility-temperature relationship of the isomers in the xylenes had to be determined. Kravchenko (*29*) had calculated eutectic points in the quaternary system of ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene, assuming the mixture to be an ideal solution, but the calculated results were slightly in error as later shown by Pitzer and Scott (*26*) who employed more precise values for the heat of fusion of the C_8 aromatics.

During development of the process used at Humble's Baytown Refinery, the solubility-temperature relationships were calculated and these data are presented in Figure 3. In calculating the solubility of individual C_8 isomers, the Van't Hoff equation, $\frac{d\ln x}{dT} = \frac{\Delta H}{RT^2}$ was integrated and theoretical composition curves were developed for various saturated solution temperatures T, where X is the mole fraction in solution and ΔH is the heat of fusion. The integration was carried out assuming that the difference in specific heats of the solid and liquid phases remained constant in the temperature range under consideration. Values for the heats of fusion employed in these calculations are given in Table III.

Table III. Heat of Fusion of C_8 Alkylbenzenes (*1*)

Compound	Heat of Fusion, Calories per Mole
Ethylbenzene	2190
o-Xylene	3250
m-Xylene	2765
p-Xylene	4090

Experimental data obtained by various workers (*26, 28*) measuring the freezing points of *p*-xylene blends in other C_8 aromatics were plotted in Figure 4 to test the reliability of calculated solubilities. The experimental points are in close agreement.

By means of these solubility curves, Figure 3, it is also possible to determine the temperature at which eutectic formation will begin. In typical xylene mixtures, either *m*-xylene or *o*-xylene may be encountered as the first eutectic depending on the composition of the mixture. A typical commercial xylenes mixture, where the concentration of *o*-xylene is 20% and *m*-xylene is 39.6%, is given in Table IV.

Table IV. Typical Composition of Solvent Xylenes

Component	Wt. %
p-Xylene	15.8
m-Xylene	39.6
o-Xylene	20.0
Ethylbenzene	18.6
Toluene	3.5
Others (paraffins, naphthenes, C_9 aromatics)	2.5

By reference to the solubility curves, it is obvious that on chilling this mixture, the saturation temperature for *p*-xylene (15.8%) is reached before the saturation value for *o*-xylene or *m*-xylene is encountered. On continued cooling, the solubility of *p*-xylene will be reached causing more crystallization of pure *p*-xylene until the next isomer, *o*-xylene, begins to precipitate as a binary eutectic. Further cooling will result in cocrystallization of *m*-xylene as a ternary eutectic when its saturation temperature is reached. Accordingly, the amount of pure *p*-xylene recoverable from this typical mixture is limited by the eutectic point and operations carried out for the production of *p*-xylene must be at a temperature level above this point. Material balances readily indicate that the yield of *p*-xylene from this mixture will be 10.1% at −98° F., the eutectic point for *o*-xylene and *p*-xylene in this mixture. Distillation of the xylenes mixture to reduce the *o*-xylene content will increase this yield slightly by reducing the temperature at which the first eutectic will be encountered. Undercutting to remove *o*-xylene may be practiced for this purpose, although Humble Oil does not employ this technique.

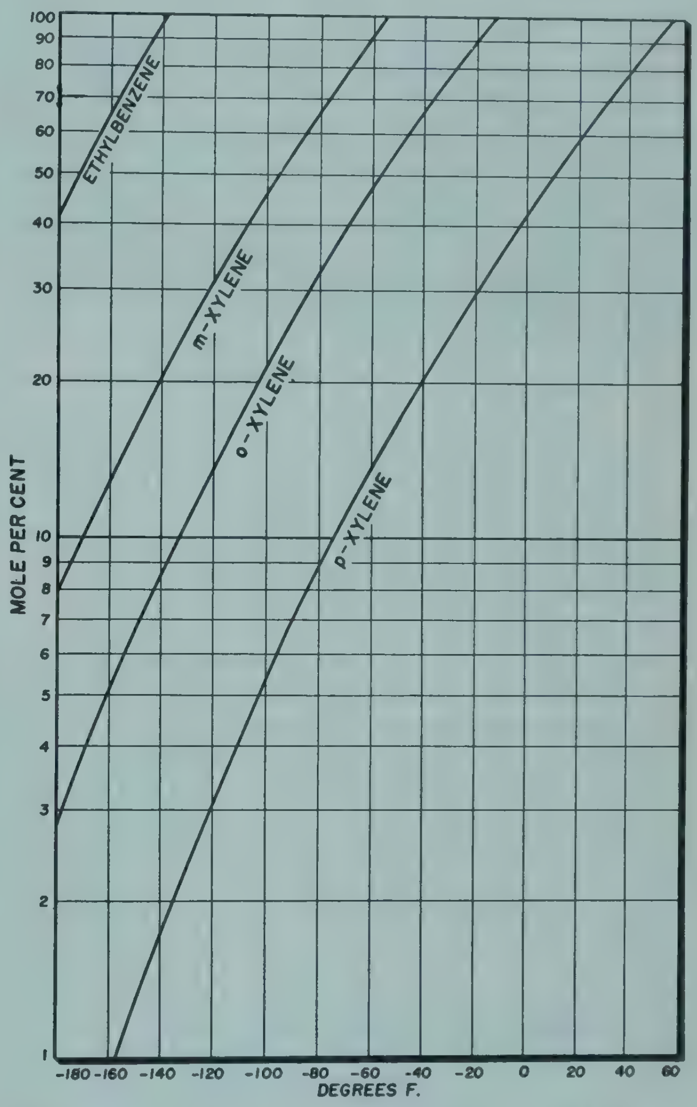
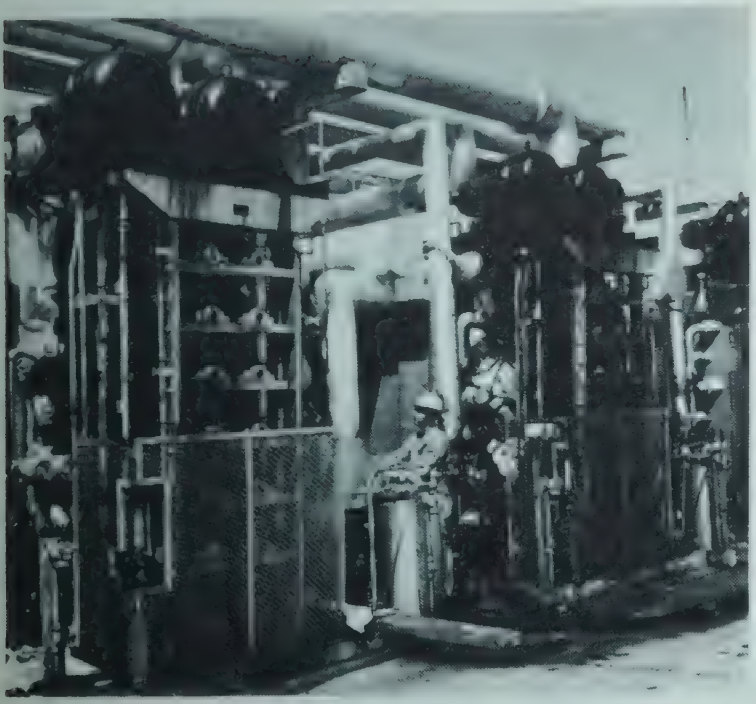


Figure 3. Solubility-temperature relationships of C_8 alkylbenzenes

Humble Oil & Refining Co. uses a two-stage process at Baytown

Humble constructed a large scale low temperature crystallization pilot plant in 1951 at its Baytown, Tex., refinery for the development of the *p*-xylene process (*4, 11*). This pilot unit was capable of producing 10,000 to 20,000 pounds per month of 95% *p*-xylene from a solvent xylenes feed stock. The purpose of the unit was threefold:



Close-up view of scraped surface chillers

To obtain engineering and process data for use in the preparation of a firm and economical plant design;

To demonstrate the operability of certain types of equipment which might be incorporated in the plant;

To prepare large *p*-xylene samples for evaluation and experimental use by potential customers.

Based on pilot plant information, a commercial plant was designed, and construction was completed in 1953. This plant was designed for the production of 25,000,000 pounds per year (226 barrels per day) of *p*-xylene, employing a two-stage crystallization and centrifugation technique. One feature of this process is that no internal refrigerants are used. In this respect, the Humble process differs from that of Standard of California, which utilizes an internal refrigerant.

The solvent xylenes feed is produced at Baytown by hydroforming virgin naphtha, fractionating the product for a xylenes distillate, and sulfur dioxide extracting the distillate for high purity xylenes. A recent analysis of solvent xylenes is shown in Table IV.

Briefly, the process involves crystallization of *p*-xylene from solvent xylenes at −95° F., followed by separation of an 80% *p*-xylene concentrate by centrifuging; this concentrate is melted, recrystallized at 0° F., and again centrifuged to produce a 95% finished *p*-xylene product. The plant flow plan is shown in Figure 2.

First crystallization stage produces 80% purity p-xylene

In the first stage the solvent xylenes feed (15.8% *p*-xylene) is pumped through a drier containing alumina for removal of water and is precooled to −35° F. with cold filtrate from the first centrifugation step in a conventional shell-and-tube heat exchanger (*3E*). This precooled feed then is chilled stepwise in two scraped surface double-walled heat exchangers (*14E*) which are refrigerated with ethylene on the shell side. This external refrigeration method of chilling the feed requires no extraneous solvent handling facilities or equipment for stripping refrigerant from the filtrate and the finished product. Ethylene for refrigeration is supplied by an electrically driven compressor (*11E*).

Since the wall of the scraped surface chiller is below the crystallization temperature of the flowing xylenes, *p*-xylene crystals deposit on the cold wall and must be removed by some means such as scraping with a spring loaded blade in order to achieve adequate heat transfer rates.

Standard of California's process eliminates the necessity for scraping interior surfaces of the chiller. Additional equipment required for separation of the internal refrigerant, however, tends to counteract the economic advantages of Standard's simplified chiller.

Referring again to the flow, the slurry is held at −95° F. for a sufficient length of time to permit a close approach to equilibrium for *p*-xylene crystallization, thereby realizing maximum *p*-xylene recovery; also, the crystals tend to grow in size in the agitated holding tank (*8E, 12E*), making the crystals more amenable to purification in a subsequent centrifuging operation. The slurry is charged from the holding tank into semicontinuous batch centrifugal filters (*1E*) for separation of the crystals from the filtrate or mother liquor. The crude crystals, containing about 80% *p*-xylene, are melted at 75° F. in a melt tank (*10E*) and are pumped to the second stage feed storage tank (*4E*). The filtrate goes to a surge tank (*6E*) and is pumped to refinery solvents storage after heat exchange with the fresh feed. All piping and process equipment operating at −20° F. or below in the first stage is constructed of stainless steel and low nickel steel.

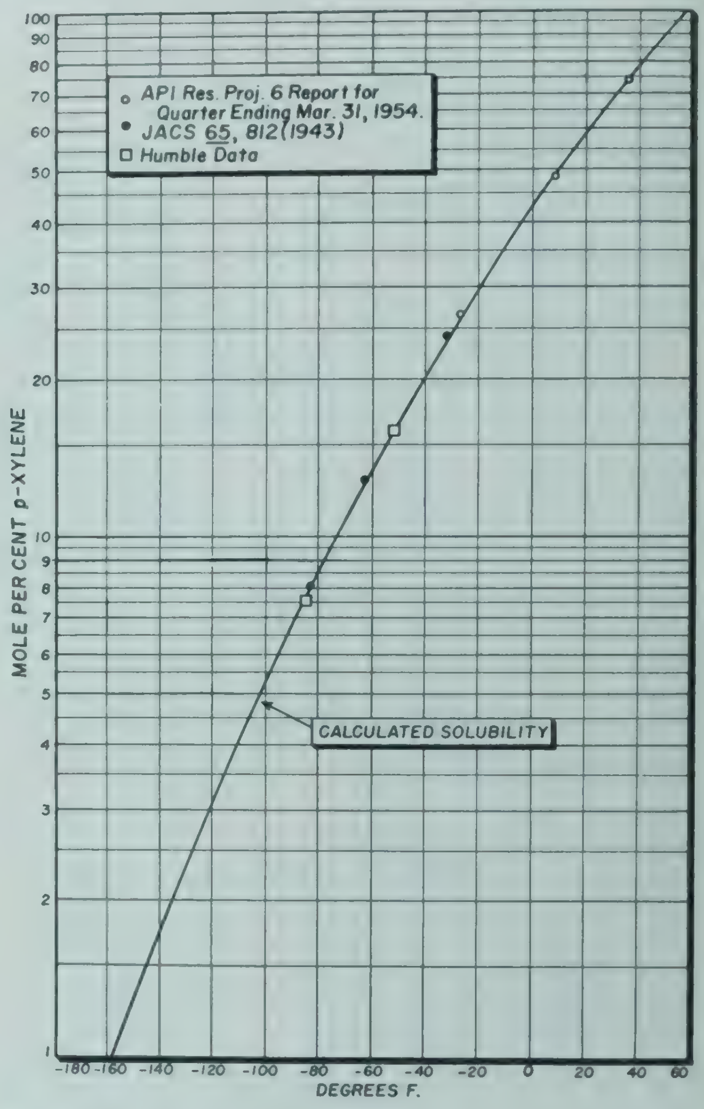


Figure 4. Measured vs. calculated p-xylene solubility

Secondary crystallization increases product purity to better than 95%

In the second stage operation, the 80% *p*-xylene concentrate produced in the first stage is precooled to 45° F. with propane in a conventional shell-and-tube heat exchanger (*2E*). This concentrate then is charged as a liquid to a scraped surface exchanger

(*13E*), refrigerated with propane. The dual service compressor that supplies the first stage operation with ethylene also provides propane for the second stage operation.

Concentrate leaving the scraped surface exchanger enters the holding tank (*7E*) at 0° F. Recrystallization at a relatively high temperature produces second stage crystals which are very large in comparison to the first stage crystals; consequently, special crystallization techniques are not necessary to attain high purities in the final centrifuging step. Crystals from the centrifuge (*1E*) are melted at 75° F. in a melt tank (*9E*) and then pumped to final product storage. The second stage filtrate, which contains about 42% *p*-xylene, goes to a surge tank (*5E*) and is recycled to the first stage for further *p*-xylene removal; as a result the yield of *p*-xylene from the feed is determined by the yield realized in the first stage.

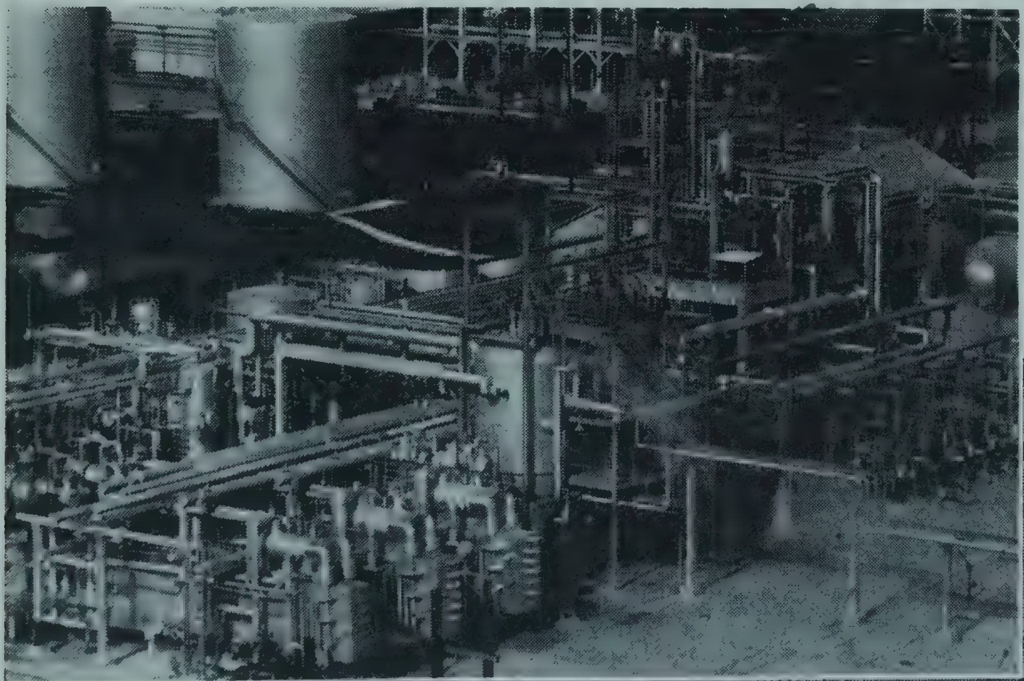
Processing the feed in two stages at different slurry temperatures permits close control of product quality at a high purity level and, at the same time, allows the realization of maximum *p*-xylene yield. Ordinarily, 95% purity product is produced, but the flexibility of the second stage operation permits the attainment of purities as high as 98%, with some reduction in yield or plant production capacity.

Product quality depends largely on crystallization techniques

Crystals may appear at −47° F. with solvent xylenes feed containing 15.8% *p*-xylene; supersaturation occurs with continued cooling, causing crystal growth if nuclei are present. For maximum *p*-xylene recovery, it is desirable to operate at the lowest possible temperature without eutectic interference.

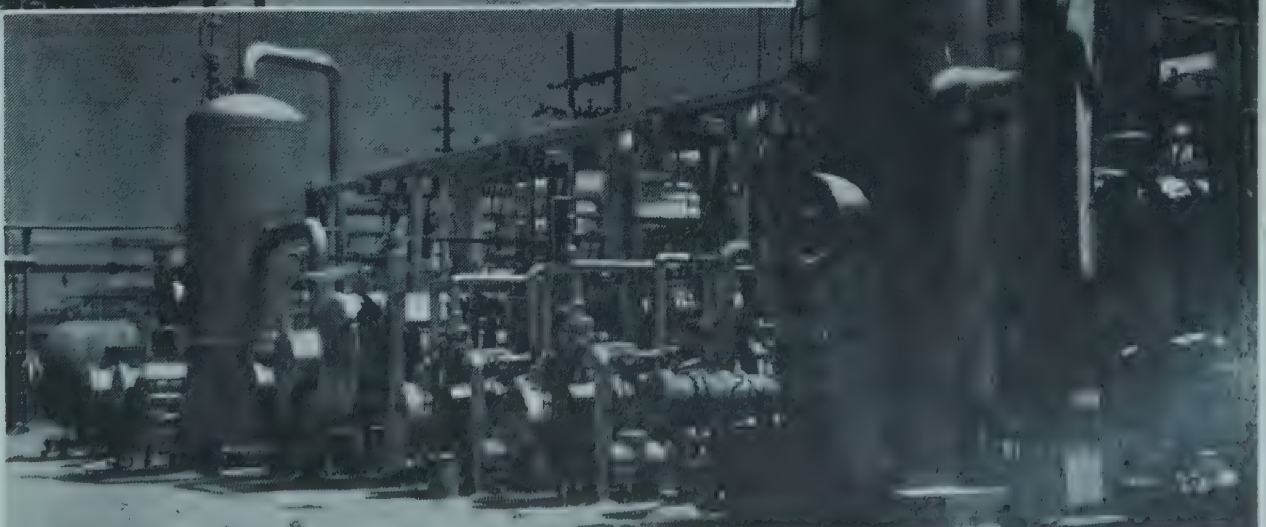
The crystallization mechanism is rather complex, involving the phenomena of diffusion, nucleation, and crystal growth occurring simultaneously. Factors exerting an influence on crystallization include the concentration of the crystallizable *p*-xylene, supersaturation, impurities, and the nature of the remaining solvent. In general, high supersaturation tends to give many nuclei, while at a low supersaturation large crystals are produced at a slow rate of growth. Nucleation may be controlled to some extent by the addition of seed crystals, and crystal growth may be regulated by the degree of supersaturation. These effects are controlled to a large degree by the stepwise manner of conducting crystallization in the first stage of the process. A cold stage microscope has been used to observe crystals produced in the first and second stage slurries. With this equipment, it was possible to estimate the crystal size and shape as well as actually make photographs of the crystals.

During the first stage of crystallization, in which the xylenes mixture is precooled to near the crystallization point in conventional exchangers and then is chilled stepwise to the operating temperature of about −95° F., crystals as illustrated in Figure 5 are produced. The primary concentrate produced in the first stage (80% *p*-xylene) is completely melted at about 75° F. and then recrystallized at 0° F. These large crystals illustrated in Figure 5,*B* differ markedly from the needlelike monoclinic type produced in the first stage, Figure 5,*A*. The average second stage



◀ **Over-all view of Humble *p*-xylene unit**

▼ **Shell and tube exchangers and knockout drums for refrigeration system**



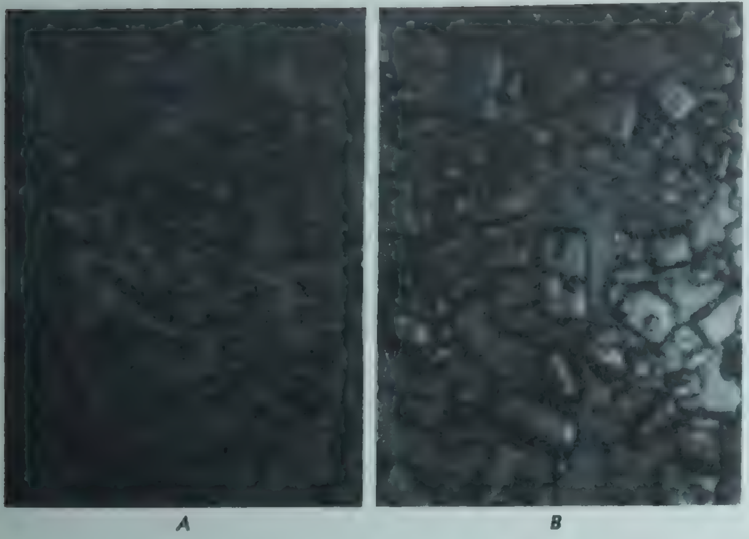


Figure 5. Large crystals produced in second stage slurry differ markedly from needlelike monoclinic type in first stage

A. First stage crystals
B Second stage crystals

crystal size is estimated at 200 by 360 microns. Complete recrystallization produces large rectangular-type crystals which can be centrifuged readily to the desired purity.

Filtration or centrifugation could be employed to separate crystals from the liquor, but automatic semicontinuous basket centrifuges are used by Humble because of their high separating force, solids handling capacity, and ability to produce a high purity product. The known factors that influence the *p*-xylene cake purity or that control the liquid drainage in a centrifuging operation are the viscosity, the interfacial tension between liquid and solid phase, the surface area of the solid phase, the free opening between the solid particles, separating force, and the distance that the liquid must travel or cake thickness. The factors of viscosity and interfacial tension are dependent only on the operating temperature since no additional solvent was used. The effect of temperature on the viscosity of the solvent xylenes at low temperatures is given in Figure 6 which shows that the viscosity increases from about 0.6 centipoise at room temperature to about 5.2 centipoise at −95° F. The size of the *p*-xylene crystals can be increased to some extent, as outlined previously, and the centrifugation process would be improved because of the smaller surface area of crystals retaining liquor and because of the larger size of the intercrystal openings.

In operating the centrifuges, the slurry containing the *p*-xylene crystals is automatically charged, and the crystals which are retained on a screen are spun to proper dryness. When the cake is dry, a knife rises automatically to cut and remove the crystals from the centrifuge bowl. The cycle is then repeated, the entire cycle being controlled automatically with electric timers. For maximum capacity, it is desirable to charge the centrifuge with slurry at a high rate, spin for as short a period as is feasible to obtain a dry cake, and discharge the cake from the centrifuge in a few seconds.

Table V. Typical p-Xylene Product

Inspections	Test Results
Freezing point, ° C.	11.53
p-Xylene, wt. %	95.7
Paraffin hydrocarbon, vol. %	Nil
Bromine No., c.g.s./cm.	0.02
Acid wash color	<1
Doctor	Sweet
Distillation range, ° C.	0.6
Halogens, wt. % as Cl	Nil
Appearance at 30° C.	Bright and clear
Saybolt color	+30
Sulfur (lamp), wt. %	0.001

As stated previously the concentration of *p*-xylene in the final product is readily controllable between 95 and 98% by adjustment of operating variables. Concentrations above 98% are attainable; however, purities in excess of 95% are not justified by current economics. Inspections of a typical product are shown in Table V.

Supply of p-xylene adequate for at least three more years

Estimates made in 1952 of the potential growth rate indicate *p*-xylene requirements may reach a level of almost 100,000,000 pounds per year by 1960 (*25*). Although there were serious setbacks to the synthetic fiber industry during 1952 and early 1953, which may delay the growth of Dacron demand, some recovery occurred during the latter part of 1953 (*18*) and during 1954. Du Pont is now pushing market outlets for Mylar film and Cronar photographic film base, in order to take up the slack in Dacron demand. In one application, Stromberg Carlson boosted its production of insulated telephone switchboard wire 35 to 46% by changing over to Mylar film as a primary insulating material. During February of this year, Du Pont announced that paper had been successfully made for the first time from synthetic fibers, using Dacron, Orlon, and nylon. Du Pont does not plan to manufacture synthetic fiber papers, although the company is making details of the work available to the paper industry.

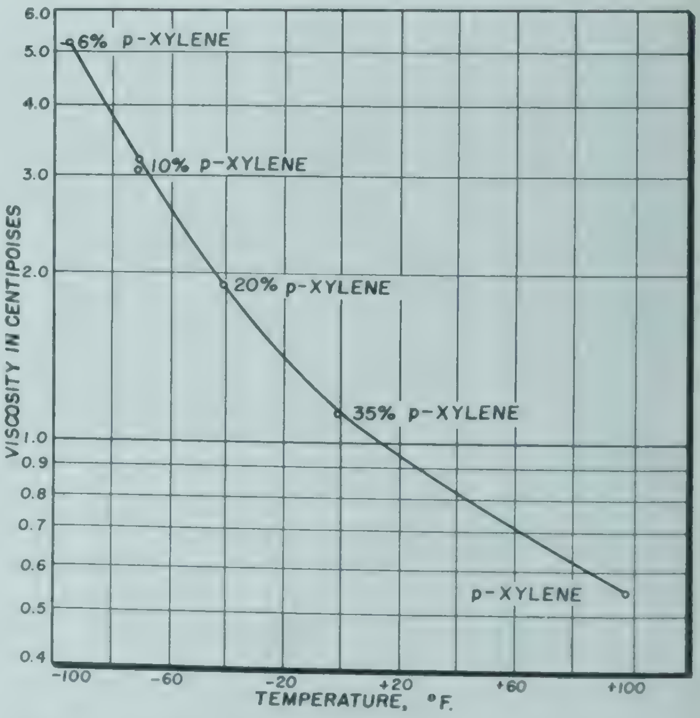


Figure 6. Effect of temperature on viscosity of solvent xylenes

Ubbelohde viscometer

It appears that the productive capacity of *p*-xylene in the United States will more than supply domestic requirements until at least 1958; another 15,000,000 or 20,000,000 pounds could easily come on stream from two major oil companies to meet all requirements until 1960. Du Pont recently lowered its estimates of Dacron consumption, indicating that nylon and Dacron may go as high as 6% of the total textile market sometime after 1960, compared with the 3% of 1954. Meanwhile, per capita fiber consumption in the United States has declined slightly from 40 pounds per year in 1950 to about 32 pounds in 1954. Du Pont foresees little change in total fiber consumption well into 1960, with a possible maximum gain of 5%.

Aside from the market outlook for *p*-xylene, which over the long term period looks favorable, technological advances in processing have been rather slow. Phillips Chemical began production of *p*-xylene in December 1953 at its new plant near Big Spring, Tex., the first process to produce a 98% product in commercial quantities. The method is reported to have other applications for liquids which are difficult to separate (*7*).

Hercules Powder manufactures dimethyl terephthalate from *p*-xylene using a new liquid phase air oxidation process, based on esterification of the monobasic *p*-toluic acid produced in the first stage and subsequent oxidation of the methyl toluate in the second stage. The process is licensed by the California Research Corp., which holds the basic U. S. patent (*22*). Hercules is understood to have made significant improvements in the process during the past two years in a development program estimated to have cost $1,500,000. The same process that converts *p*-xylene to dimethyl terephthalate can produce dimethyl isophthalate from a feed of mixed xylenes (70 to 80% meta, the remainder para). Hercules is still operating a pilot plant producing 120,000 pounds per year of dimethyl isophthalate from meta and mixed xylenes. The only large scale plan for pure meta conversion is Oronite's $10-million plant for isophthalic acid production now under construction at Standard of California's refinery in Richmond, Calif. (*12, 15*). Unlike Hercules, Oronite plans to market the acid rather than the dimethyl ester. The first large commercial supplies of technically pure (95+%) *m*-xylene in the United States will also be offered by Oronite on completion of this new plant. Richfield Oil Co. is operating a pilot plant unit at its Watson, Calif., refinery for the production of phthalic acids by the oxidation of xylenes, but the company's plans for commercial developments are as yet unknown.

Significant increases in the demand for *p*-xylene could bring about technical changes in processing, if the demand should exceed either the market for ortho and meta isomers, or the market for mixed xylenes as a solvent. One alternative would be isomerization of the mixed xylenes leaving the crystallization process for recycling and additional *p*-xylene recovery. Another possibility is the use of solid compound formation (*15, 17*), a California Research Corp. technique designed to boost para recovery through the use of carbon tetrachloride.

Possible production of terephthalic acid from butylene has been pointed out in some German work on reactions catalyzed with lithium aluminum hydride. In this process, yields of over 50% *p*-xylene are obtained with ethylbenzene and *o*-xylene as the only other products. Since separation of these materials is much easier than separating the three isomeric xylenes, this process, in which the hydride is a "true" catalyst and is not consumed, has real commercial possibilities.

Recent European work, in which terephthalic acid is derived by isomerization of phthalic anhydride, opens an attractive direct route that eliminates the *p*-xylene recovery step, but this process has not been employed on a commercial scale in the United States.

Acknowledgment

The authors are grateful to Humble Oil & Refining Co. for the opportunity to prepare and publish this information. Acknowledgment is made, also, of the technical contributions of R. F. Pfennig and R. A. Speed of Humble, and others who assisted in the development of this process. Other helpful technical assistance was obtained from Esso Research and Engineering Co. through a research contract.

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Processing equipment

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(2E) C. F. Braun & Co., Alhambra, Calif., carbon steel shell-and-tube heat exchanger.
(3E) *Ibid.*, low temperature alloy shell-and-tube heat exchanger.
(4E) *Ibid.*, carbon steel feed tank, 20,000-gallon.
(5E) *Ibid.*, carbon steel filtrate surge tank, 1000-gallon.
(6E) *Ibid.*, 304 stainless steel filtrate surge tank, 7500-gallon.
(7E) *Ibid.*, carbon steel holding tank.
(8E) *Ibid.*, 304 stainless steel holding tank.
(9E) *Ibid.*, carbon steel melt tank, 400-gallon.
(10E) *Ibid.*, carbon steel melt tank, 10,000-gallon.
(11E) Clark Bros. Co., Inc., Olean, N. Y., electrically driven compressor (propane-ethylene service), 600 hp. "Right Angle" 2-cycle.
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In Aluminum Production the First Stage Is

ALUMINA

KENNETH M. REESE, Assistant Editor in collaboration with
W. H. CUNDIFF, Kaiser Aluminum & Chemical Corp., Oakland, Calif.

ALUMINUM, the most abundant metallic element in the earth's crust, was isolated first in 1825 by the Danish chemist Oersted (*2*) who heated potassium amalgam with aluminum chloride and distilled the mercury from the resulting aluminum amalgam. This was quite an accomplishment, since Davy had tried earlier to obtain aluminum and had failed. The German, Wöhler, isolated aluminum in 1827 by heating metallic potassium with aluminum chloride. Wöhler was never able to get the resulting aluminum particles to coalesce (because of their accompanying oxide film), but he did work out the first data on the metal's physical and chemical properties.

Industrial aluminum got its first toehold in 1854 with Saint-Claire Deville's substitution of sodium for potassium in Wöhler's method. Deville found that sodium chloride from the aluminum chloride reduction reacted with excess aluminum chloride to give a fusible double chloride of sodium and aluminum, and that this salt acted as a flux which allowed the aluminum globules to coalesce. Deville interested the French Academy and Napoleon III in his process, and in 1856, following further development work, aluminum manufacture began for the first time in a small plant near Paris.

At this point aluminum was still a very costly metal, so costly, in fact, that Napoleon III used an aluminum dinner service at important state functions. Improvements in the Deville process and substantial reductions in the cost of sodium (to $1.00 a pound) dropped the price of aluminum to $17 a pound by 1859. Others were crowding into the field by this time, but while process improvement was steady, economical volume production of aluminum lay still some distance in the future.

Hall and Bayer find the answers

The breakthrough came in 1886 when Hall in America and Heroult in France found independently that aluminum oxide, dissolved in molten cryolite, could be decomposed electrolytically without decomposing the cryolite (*4*). In 1888, the Austrian, Bayer, perfected his method for treating bauxite to get purified alumina (*1*), the raw material for the Hall-Heroult reduction pots. While the Hall-Heroult and Bayer processes have undergone much refinement and some modification, they still account for virtually all of the primary aluminum made in the world.

Once on its feet, aluminum moved ahead rapidly (Table I). It boasts some 4000 end uses today and tops all other nonferrous metals in production volume. Aluminum is very light, with a specific gravity of 2.70 compared to 7.86 for iron. It has low strength in the pure state but can be alloyed to give a tensile strength greater than that of mild steel. It is durable, will not rust, and resists many chemicals (except alkali) very well. Aluminum can be formed by most of the common metal working techniques and can be welded, brazed, and soldered. It has high thermal and electrical conductivity and is a good reflector of light and radiant heat. It is an extremely versatile metal.

Bauxite, the principal ore of alumina (Table II), occurs in many parts of the world, and known world reserves total more than 1,600,000,000 tons. The North American aluminum industry depends chiefly on deposits in Dutch Guiana (Surinam), British Guiana, Jamaica, and the state of Arkansas. Improved technology is expanding these sources continually. At one time, for example, it was not economical to process bauxite containing more than 7% silica. On this basis, U. S. domestic reserves totaled 9,300,000 tons in 1941. Development of a modified Bayer process, however, made possible economical processing of bauxite containing up to 15% silica, thus effectively increasing domestic reserves to 50,000,000 tons today, exclusive of the 25,000,000 tons mined in the interim.

After the rediscovery of Jamaican bauxite in 1942, it was found that this bauxite could be processed in existing American Bayer plants only with difficulty. Subsequent developments in processing methods minimized some of the problems, and Jamaican bauxite is now a major source of alumina in both the United States and Canada. Useful Jamaican reserves have been estimated to be 315,000,000 metric tons containing 67,000,000 metric tons of aluminum (*6*). These Jamaican reserves represent 20% of the known free world reserves of bauxite and contain recoverable metal equivalent to 50 times the 1954 production of primary aluminum in the United States.

Cryolite, chief constituent of the alumina reduction bath, will soon come entirely from synthetic sources, since the only commercial, natural source (in Greenland) is nearly depleted. Acid-grade fluorspar, the main source of fluorine for synthetic cryolite, was recently in short supply, but this shortage has been relieved. Also, phosphate rock holds the largest known fluorine deposits, and at least one U.S. fertilizer company lists cryolite and aluminum fluoride among its by-product sales items.

Table I. Primary Aluminum Production and Capacities[a]

(Thousands of short tons)

Year	U. S.	World
1910	18.0	41.9
1920	69.0	170.1
1930	114.5	295.5
1940	206.3	902.8
1950	718.6	1647.9
1951	836.9	1973.1
1952	937.3	2258.9
1953	1252.0	2717.2
1954	1461.0	3400.0 (est.)

North American Producers	Capacity, Thous. Short Tons/Year
Aluminum Co. of America (Alcoa)	653.8
Aluminum Co. of Canada (Alcan)	550.0
Reynolds Metals Co.	414.5
Kaiser Aluminum & Chemical Corp.	408.0
Anaconda Aluminum Co.	60.0

[a] Sources: U. S. Bureau of Mines, Aluminum Assoc., Metal Statistics.

Kaiser enters the aluminum business, 1946

Kaiser Aluminum & Chemical Corp. entered the aluminum business in 1946 when it leased from the Government the Baton Rouge, La., alumina plant, the Mead, Wash., reduction plant, and the Trentwood, Wash., sheet and plate rolling mill. In 1947, Kaiser bought the Tacoma, Wash., reduction plant. In 1949, the corporation purchased, with private capital, the three plants originally leased and the Newark, Ohio, rod and bar mill, which it equipped to make wire and electrical conductor as well. In 1949, also, Kaiser Aluminum established at Permanente, Calif., the first foil mill west of St. Louis, and two years later acquired an extrusion plant at Halethorpe, Md.

In 1951, the corporation launched a privately financed expansion program totaling more than a quarter of a billion dollars, climaxed by completion of the giant Chalmette, La., reduction plant. The program also included acquisition and development of some 30,000 acres of Jamaican bauxite reserves, from which the first shipments went out in 1953, expansion and modification of the Baton Rouge alumina plant, and expansion of other facilities. A multi-million dollar aluminum sheet and foil mill is currently under construction at Ravenswood, W. Va. In 1954, the corporation leased an aluminum forging plant at Erie, Pa., and recently was awarded a contract by the Air Force to operate an extrusion plant containing two 8000-ton presses under the Air Force heavy press program.

Table II. Typical Bauxite Analyses

	Jamaican, %	Surinam, %	Arkansas, %	European, %
Al_2O_3				
Gibbsite	38	52.5	40	
Boehmite	9			53
Kaolinite, etc.	2	3	10	4
Fe_2O_3	20	9	8	24
SiO_2	2.5	3.5	12	5
TiO_2	2.5	2.5	3	2
Minor constituents	1.0	0.5	1	0.5
Loss on ignition	25	29	26	11.5

Kaiser Aluminum now has a rated primary aluminum capacity of 408,000 tons a year, or close to 30% of the total U. S. capacity. (The company's Chemicals Division operates three plants in California, which produce dolomite, seawater magnesias, and basic refractories, and is constructing a basic refractories brick plant for $4,000,000 at Columbiana, Ohio.)

Kaiser's Jamaican bauxite facilities, installed at a cost of $17,000,000, can turn out more than 1,500,000 tons of ore a year. Ore is strip mined and dried to 15% moisture in rotary, oil-fired driers. As mined, Jamaican bauxite contains about 20% moisture and, upon continued handling, becomes sticky and difficult to manage. At 15% moisture it can be handled satisfactorily, and drying costs and increasing fines losses militate against drying below this point. After drying, the bauxite goes aboard 10,000-ton, general cargo vessels for the 1100-mile trip to the Baton Rouge alumina plant. Kaiser Aluminum also uses Surinam ore, for which it has a contractual obligation extending through 1963.

The Baton Rouge alumina plant is located on the east bank of the Mississippi. It is accessible to ocean going vessels and is close to the mid-southern alkali industry and large natural gas reserves. Completed in 1943 at a cost of $18,000,000, it has been modified and expanded at an additional cost of $28,000,000 to an alumina capacity of more than 800,000 tons per year. It supplies all the alumina for Kaiser's reduction plants and produces also a number of alumina products for use in the chemical, refractories, and abrasives industries.

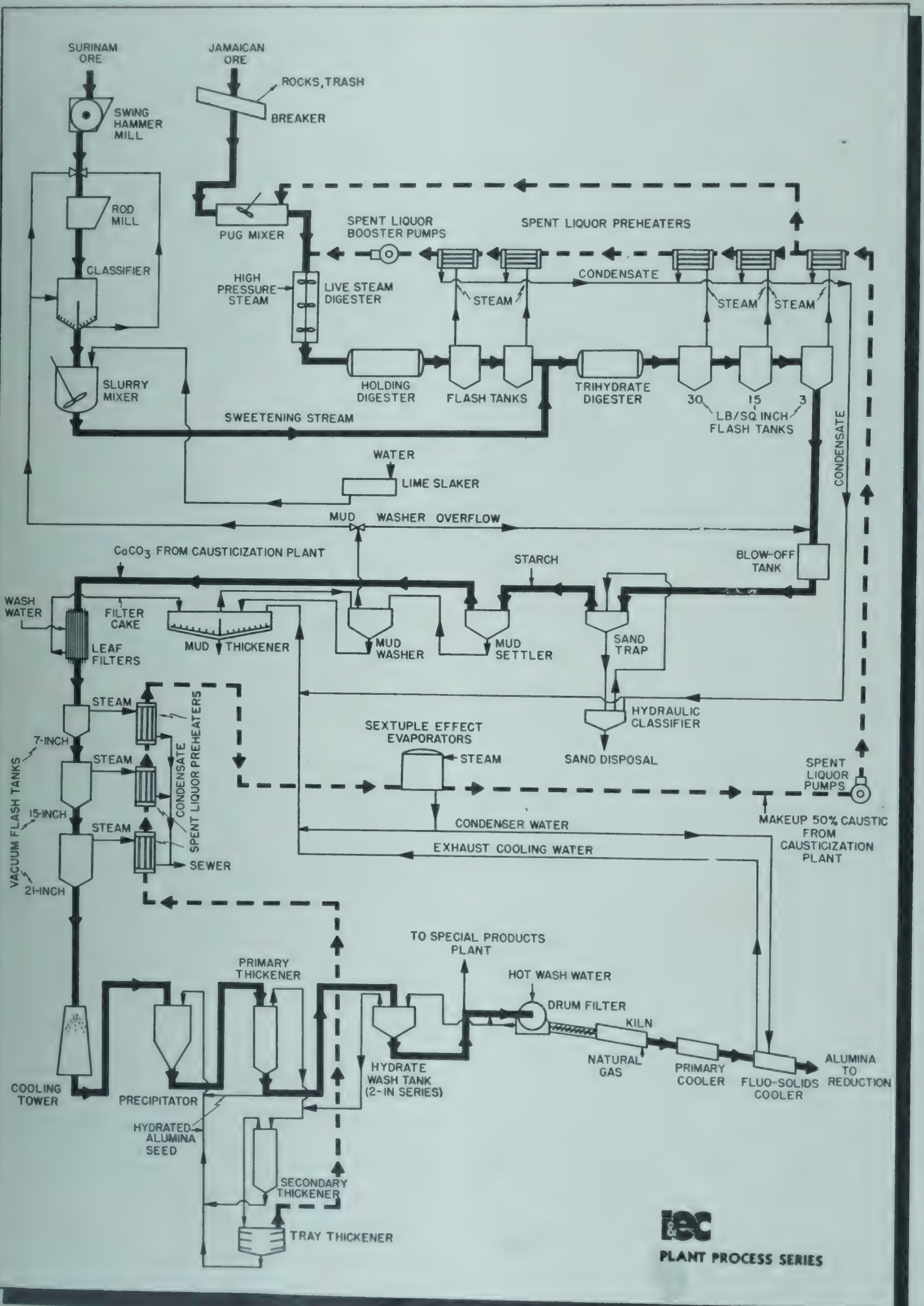

SURINAM ORE
JAMAICAN ORE
ROCKS, TRASH
BREAKER
SWING HAMMER MILL
ROD MILL
PUG MIXER
SPENT LIQUOR BOOSTER PUMPS
SPENT LIQUOR PREHEATERS
CLASSIFIER
HIGH PRESSURE STEAM
LIVE STEAM DIGESTER
CONDENSATE
STEAM
STEAM
STEAM
STEAM
SLURRY MIXER
HOLDING DIGESTER
FLASH TANKS
TRIHYDRATE DIGESTER
30
15
3
LB/SQ. INCH FLASH TANKS
SWEETENING STREAM
CONDENSATE
WATER
LIME SLAKER
MUD WASHER OVERFLOW
$CaCO_3$ FROM CAUSTICIZATION PLANT
STARCH
BLOW-OFF TANK
WASH WATER
FILTER CAKE
LEAF FILTERS
MUD THICKENER
MUD WASHER
MUD SETTLER
SAND TRAP
STEAM
HYDRAULIC CLASSIFIER
7-INCH
STEAM
SEXTUPLE EFFECT EVAPORATORS
STEAM
SAND DISPOSAL
VACUUM FLASH TANKS
15-INCH
STEAM
CONDENSATE
SPENT LIQUOR PREHEATERS
SPENT LIQUOR PUMPS
CONDENSER WATER
MAKEUP 50% CAUSTIC FROM CAUSTICIZATION PLANT
21-INCH
SEWER
EXHAUST COOLING WATER
TO SPECIAL PRODUCTS PLANT
PRIMARY THICKENER
HOT WASH WATER
DRUM FILTER
KILN
NATURAL GAS
PRIMARY COOLER
FLUO-SOLIDS COOLER
ALUMINA TO REDUCTION
COOLING TOWER
PRECIPITATOR
HYDRATE WASH TANK (2-IN SERIES)
HYDRATED ALUMINA SEED
SECONDARY THICKENER
TRAY THICKENER
I&EC
PLANT PROCESS SERIES

Figure 1. Flow sheet for production of alumina from bauxite at the Baton Rouge, La., plant of Kaiser Aluminum & Chemical Corp.

Table III. Comparison of Sweetening Process with Single Digest Processes of Jamaican Bauxites[a]

	Single Digest Process		Sweetening Process Two Step
	Mono-hydrate	Tri-hydrate	
Bauxite	2.3	2.7	2.42
Spent liquor alumina to caustic soda ratio	0.320	0.320	0.320
Monohydrate digester conditions			
Temperature, ° F.	400	...	390
Caustic concentration, grams/liter	260	...	200
Alumina to caustic soda effluent ratio	0.600	...	0.560
Trihydrate digester conditions			
Temperature, ° F.	...	290	300
Caustic concentration, grams/liter	...	170	210
Alumina to caustic soda effluent ratio	...	0.640	0.650
Digester liquor heater steam	0	0.60	0
Digester injection steam	2.64	0.9	2.0
Total digestion steam	2.64	1.5	2.0
Evaporation required	11	3	5

[a] Amounts of bauxite, steam, and evaporation are given in pounds per pound of Al_2O recovered.

Baton Rouge uses modified Bayer process

The Baton Rouge alumina plant uses the "sweetening" process (*5*), a modification of the Bayer process developed by Kaiser Aluminum's Research and Development Division. The Bayer process itself depends in part upon the fact that the alumina in bauxite can be dissolved in caustic by digestion at elevated temperature and pressure. European bauxite contains massive monohydrate alumina (boehmite) which extracts very slowly, and is commonly digested at about 390° F., a pressure of 210 pounds per square inch, and at a caustic concentration of 400 grams per liter (in the digester feed), as follows:

$$Al_2O_3.H_2O + 2NaOH \rightarrow 2NaAlO_2 + 2H_2O$$

Surinam bauxite, on the other hand, contains trihydrate alumina (gibbsite), which allows it to be digested at about 290° F., a pressure of 60 pounds per square inch, and at a caustic concentration of 170 grams per liter (in the digester feed), as follows:

$$Al_2O_3.3H_2O + 2NaOH \rightarrow 2NaAlO_2 + 4H_2O$$

Jamaican bauxite, however, contains significant amounts of both boehmite and gibbsite. Unlike European bauxite, Jamaican bauxite, including its boehmite, extracts rapidly because it is very finely divided in its natural state, the average particle size being substantially less than 1 micron.

Standard trihydrate digestion as practiced in America could be used on Jamaican bauxite, but appreciable loss of unextracted monohydrate alumina would result. Standard European monohydrate digestion would extract all the alumina, but even these temperatures, pressures, and caustic concentrations would not give the high alumina concentrations common in America.

Kaiser Aluminum's solution to this problem consists basically of an initial monohydrate digest. To this stream is added the sweetening stream containing trihydrate bauxite. The mixture is then subjected to a trihydrate digest. The sweetening process is highly flexible in regard to the type of ore used, and for straight Jamaican bauxite offers significant advantages over a single monohydrate or trihydrate digest (Table III). While the process as described below is based on partial use of Surinam bauxite, it can operate economically on a 100% Jamaican bauxite charge.

Iron oxide and titania in the bauxite pass unaffected through digestion and are discarded with the insoluble residue (red mud). Silicates form an insoluble sodium-aluminum complex during digestion. This product, probably $3Na_2O.3Al_2O_3.5SiO_2 5H_2O$ leaves with the red mud, and represents the major alumina and caustic loss. This loss can be tolerated with Jamaican and Surinam ores but becomes serious with high silica Arkansas bauxite. Arkansas bauxite users (Alcoa at Bauxite, Ark., and Reynolds at Hurricane Creek, Ark.) employ a lime-soda sintering process (*3*) to recover the alumina and caustic that otherwise would leave as complex silicates with the red mud.

Sodium aluminate solution goes from the digesters to a series of flash tanks which discharge it at atmospheric pressure. One of the important and unique principles of the Bayer process is that the pregnant liquor, called green liquor in the industry, is highly supersaturated and yet very stable in the absence of hydrated alumina crystals. Thus, a green liquor from the digestion system contains 120% of the alumina representing saturation concentration for that liquor. It is then subjected to sedimentation, filtration, and vacuum-flash cooling which increases the degree of supersaturation to more than 200%. When all of this is done in the absence of hydrated alumina seed particles, the liquor remains stable and no alumina is lost from the solution. The introduction of seed crystals into the liquor upsets the metastable system, and hydrated alumina then precipitates from the solution:

$$2NaAlO_2 + 4H_2O \rightarrow Al_2O_3.3H_2O + 2NaOH$$

Precipitation is relatively rapid at first but slows as the system approaches equilibrium which would correspond to about 40% of the original dissolved alumina. Process economics at the Baton Rouge plant dictate that about 50% of the alumina be recovered from the liquor each cycle. The other half is recycled with the spent liquor stream returning to the digesters. En route, the spent liquor is preheated by steam generated from cooling the green liquor stream.

Ore ships unload directly at plant site

Two 12-ton cranes unload the 10,000-ton bauxite vessels in 30 to 33 hours at a 500-foot dock. Bauxite goes to storage on 36-inch belt conveyors at a maximum rate of 900 tons per hour. Jamaican bauxite arrives in an earthy agglomerate form; because of its poor handling quality if allowed to get wet it is stored in a building with capacity of 90,000 tons. Surinam bauxite arrives in 2-inch lumps and smaller and is stored out of doors.

Jamaican bauxite from storage need not be crushed, but it contains limestone rocks that originate in the ore bed. These and other extraneous matter are removed by a breaker at rate of 250 tons per hour (*16E*) with 5/8-inch openings (Figure 1).

The bauxite moves to three slurrying units arranged in parallel; each is made up of a relay bin, an automatic weigher (*15E*), and a pug mixer of 70 tons per hour (*14E*). There are also two spare slurrying units. Besides bauxite, the pug mixers are fed spent liquor (Table IV); the flow is adjusted to give a 50% slurry out of the slurrying units. Pug mixer agitation must be gentle. Otherwise the Jamaican bauxite agglomerates would break down into submicron size particles yielding a viscous slurry which would be increasingly hard to handle with continued agitation.

Table IV. Operating Conditions at Kaiser Baton Rouge Alumina Plant

	Caustic Concentration[a], Grams/Liter	Alumina to Caustic Ratio[a]	Temperature, ° F.
Spent liquor entering pug mixers	235–255		200
Spent liquor to line feeding live steam digesters	235–255		300–320
Monohydrate digesters	190–210	0.520:0.580	380–400
Trihydrate digesters	190–210		285–300
Blow-off tank underflow	165–175		215
Green liquor feed to precipitators	170–180	0.630:0.650	155–170
Spent liquor leaving tray thickeners	175–185	0.310:0.340	130–140
Spent liquor leaving evaporators	230–260		145–170

[a] In the U. S. alumina industry, caustic concentration is the sodium carbonate equivalent of the sum of the sodium aluminate and free sodium hydroxide. Alumina to caustic ratio is the weight ratio of dissolved alumina to caustic.

Flash and digestion tanks

Flash tanks (left) supply steam to sheet-and-tube heat exchangers; digestion tanks are at right

Jamaican slurry is joined by more spent liquor, and steam-driven, reciprocating pumps (*20E*) charge the combined stream to three live-steam digesters, 8 feet in diameter and 30 feet long which are arranged in parallel and have mild agitation. There are also two spare live steamers. Attainment of digester working temperature requires injection of 110,000 to 140,000 pounds per hour of steam at 300 pounds per square inch for each operating digester unit. The holding time in this vessel is arranged to localize as much as possible the deposition of sodium aluminum silicate scale. During the 5-minute holding time in the live steamer, most of the silica is converted to insoluble sodium aluminum silicate, a large part of which leaves the system with the red mud. It does form some scale in these vessels, which necessitates a descaling cycle of 30 to 60 days.

The process stream then enters three monohydrate digestion units arranged in parallel. Each unit contains two holding digesters, which have mild agitation and are arranged in series. Total holding time in the two holding digesters (10 feet in diameter and 60 feet long) is 30 to 40 minutes, and pressure (225 pounds per square inch) is 25 to 30 pounds per square inch above liquor vapor pressure at this point. After digestion, the charge is flashed in two stages to a temperature range of 300° to 320° F. in two flash tanks whose pressures are held between 90 and 120 pounds per square inch and 45 and 65 pounds per square inch, respectively. The second flash tank is elevated (to get the proper pressure head) and operated so as to maintain working temperature and pressure in the trihydrate digesters which are next in line. Steam made in the flash tanks goes to spent liquor preheaters. Before the process stream enters the trihydrate digesters, it is combined with the sweetening stream which originates in the Surinam slurrying units.

Surinam bauxite from storage is crushed to $-{}^1/_2$ inch by two swing-hammer mills at 200 tons per hour (*17E*). Crushed bauxite goes to three slurrying units arranged in parallel; each is made up of a storage bin, a relay bin, a weigh-batcher, a rod mill of 50 tons per hour (*1E*), a rake classifier (*5E*), and a slurry mixer. There is also a spare slurrying unit. The rod mill and classifier, which operate in closed circuit, are also fed mud washer overflow. The classifier overflow is a 30% slurry of bauxite (99% −20 mesh) which is mixed in the slurry mixer with a 20% slurry of hydrated lime. Phosphate in the Jamaican bauxite reacts with this lime in the trihydrate digesters to precipitate calcium phosphate. If phosphate were not so precipitated, it would contaminate the product alumina; the net result would be lowered efficiency in the aluminum reduction pots. Jamaican bauxite now used analyzes about 0.25% phosphate; Surinam ore contains about one fifth of this amount and does not pose a phosphate problem.

Main and sweetening streams meet

At this point the sweetening stream from the Surinam slurrying units meets the main stream from the monohydrate digestion units, and the combined stream enters three trihydrate digestion units arranged in parallel. Each unit contains three digesters which are arranged in series and have mild agitation; there are also spare digester vessels in each unit. The digesters are 8 feet in diameter and 30 feet long, and digestion pressure (55 to 70 pounds per square inch) is about 20 pounds per square inch above liquor vapor pressure. Caustic concentration (190 to 210 grams per liter) is higher than required for extraction of the trihydrate alumina but is predetermined by the over-all process material balance.

After a digestion of 15 to 25 minutes, the liquor is flashed in three sets of flash chambers made up of three flash chambers per set. The liquor flashes consecutively to nominal pressures of 30, 15, and 3 pounds per square inch and then drops to atmospheric pressure in the blow-off tanks. Steam made in the flash tanks goes to spent liquor preheaters.

Each blow-off tank is fed approximately 2000 gallons per minute of digester effluent and 1000 gallons per minute of mud washer overflow. Blow-off tank underflow, now ready for clarification, contains 3 to 4% of finely divided solids composed of oxides of iron and titanium and desilication product.

The first clarification unit is a sand trap which takes out +28-mesh particles; it operates in closed circuit with a rake classifier (*6E*). Sand trap overflow flows by gravity to 10, four-compartment, 35-foot mud settlers (*8E*) and two 40-foot settlers of the same type; one settler is always offstream for cleaning. Mud settler overflow goes to the filters. Settler underflow, at 15 to 20% solids, goes to six-compartment, five-stage, countercurrent decantation mud washers (*10E*); there are nine such washers, 55 feet in diameter and 60 feet high. The mud washer underflow is sent to a mud thickener for final washing before disposal. The wash water is added to the thickener at the rate of 9 to 12 pounds of water per pound of dry solids. Mud thickener overflow is pumped back to the mud washers. The wash water rate is relatively high compared with that used in the treating of trihydrate bauxite but is necessary to maintain the water balance in the process. This high rate is also advantageous from the mud washing point of view, as it gives thorough removal of caustic from the mud.

Starch is used to aid settling of the finely divided mud particles that result when Jamaican bauxite is processed. Kaiser Aluminum uses 0.007 pound of starch per pound of mud. Settling is further improved by recycling part of the mud washer overflow to the blow-off tanks. This reduces caustic concentration in the mud settler feed. The remainder of the mud washer overflow goes to the Surinam slurrying units.

Mud washer underflow, at 15 to 20% solids, discharges to the mud thickener, an earth-fill bowl with a rake of 150 feet in diameter and center pier driven. Wash water to the mud thickener is supplied by exhaust cooling water from the calcined alumina fluo-coolers and evaporator condenser water. Thickened mud is produced at about 1800 tons of solids per 24 hours.

Pressure leaf filters further clarify green liquor

Green liquor overflow from the mud settlers is pumped to 48 pressure leaf filters (*11E*) which include spares and operate at 25 to 35 pounds per square inch. Each filter has an effective area of 927 square feet of 16-ounce duck, and calcium carbonate from the causticizing operation is used as a filter aid. The filter cloth may harden gradually because of premature alumina deposition and gradually deteriorates because of oxidation catalyzed by the caustic. Thus, the cloth must be removed and discarded at a rate of about 0.3 square yard per ton of product alumina. Filter cake is sluiced hydraulically from the filters. Green liquor enters the filters at 200° F., containing 50 to 100 mg. of suspended solids per liter. Filtrate flow per filter is 250 to 300 gallons per minute containing less than 20 mg. of solids per liter.

Clarified green liquor is pumped to three sets of vacuum flash tanks arranged in parallel; each set is made up of three tanks operating at 7, 15, and 21 inches of mercury vacuum. Steam made in these flashers goes to spent liquor preheaters. After flashing, the green liquor, now at 170° F., is sprayed into three atmospheric cooling towers, 50 feet in diameter and 30 feet high, which cool it to precipitator filling temperature.

There are 139 precipitator tanks, 24 feet in diameter and 60 feet high; they have open tops and 90-degree cone bottoms. Some tanks are always down for scaling and some act as service tanks. Precipitators are filled to within 10 to 15 feet of the top, slurried alumina hydrate seed is charged, and the tank is then topped off with more green liquor. This method avoids the possibility of charging too much liquor and then overflowing the tank with the seed charge.

A typical precipitator charge is 180,000 gallons of liquor plus 75,000 pounds of tray thickener seed (dry basis), or 150,000 pounds of secondary thickener seed, or 250,000 pounds of primary thickener seed. These weights give equal amounts of precipitation per tank charged. An air lift mounted along the precipitator center line holds the seeds in suspension but provides no violent agitation. During the precipitation cycle, which may vary from 36 to 48 hours, about half of the dissolved alumina precipitates onto the seed. In a 24-hour day, each working precipitator turns out 31 to 38 tons of alumina hydrate, equivalent to 20 to 25 tons of product alumina.

Mud thickener, a 150-foot diameter earth-fill bowl, processes about 1800 tons of mud solids per 24 hours

Precipitation is difficult art

Alumina precipitation is a critical and difficult art. Kaiser, for instance, says that while it precipitates about 50% of the alumina that enters the tank, this amount could be increased significantly if the pertinent variables could be controlled more precisely. Hydrate particle size distribution is important since a certain size range is wanted in the product and another in the seed. Therefore, temperature, seed charges, and concentrations are adjusted to give an economic balance between the weight of product and the weight of seed produced during the precipitation period. The more alumina precipitated, the less the amount of alumina and caustic that must be continuously recycled, and the lower the process heat and handling cost per ton of product. But on the other hand, the lower the alumina to caustic (finishing) ratio, the finer the particles produced. On these bases, Kaiser Aluminum operates its precipitators at the lowest finishing ratio consistent with satisfactory particle size distribution. Control of the particle size distribution is accomplished by operating the system with a small deficiency of fine seed. Thus some product size hydrate is used to make up this deficiency. Control of the particle size distribution becomes much more difficult and critical as the system approaches an exact balance between fine seed produced and fine seed required.

Precipitator effluent goes to six primary thickeners (*3E*) which are 24 feet in diameter and 60 feet high and have feed wells of 10 feet in diameter. Primary thickener underflow contains 55% solids (alumina hydrate product) which average 50% +200 mesh and 90% +325 mesh. The overflow passes to five secondary thickeners (*4E*) which are 40 feet in diameter, 50 feet high, and have feed wells of 20 feet in diameter. Secondary thickener underflow contains 45% solids which average 20% +200 mesh and 70% +325 mesh; it is used as produced to seed the precipitators. Overflow goes to 10 three-compartment tray thickeners (*9E*), 50 feet in diameter and 24 feet high. Tray thickener underflow contains 30% solids which average 30% +325 mesh. It, too, is

Rotary kilns

Washed alumina hydrate is calcined at 2000° F.

used to seed the precipitators. Tray thickener overflow, containing less than 1 gram of suspended solids per liter, is the spent liquor.

Spent liquor is recycled

Spent liquor is pumped from the tray thickeners to three sets of preheaters arranged in parallel. Each set contains three shell-and-tube heat exchangers, 600 tubes and eight passes (*2E*), arranged in series plus one spare heat exchanger. These preheaters are fed steam from the three sets of vacuum flash tanks just ahead of the cooling towers; they heat the spent liquor from about 135° to 170° F., at which temperature it goes to the evaporating plant to be concentrated.

Six sextuple effect units make up the evaporating plant. Four of them (*12E*) can evaporate 200,000 pounds of water per hour each and two (*13E*) can evaporate 150,000 pounds per hour each, giving a total evaporating capacity of 1,100,000 pounds an hour. Feed liquor to the four large evaporators is split, one half going to the hot end and the other half to the cold end. From this point the large evaporators operate uniquely in that the hot and cold end streams meet between the third and fourth effects, where final concentration is carried out in successive, external flashers at 14, 20, and 26 inches of mercury vacuum. This arrangement allows salts that precipitate during final concentration to deposit in the flash tanks instead of on heat transfer surfaces in the evaporators. Furthermore, the flash tanks can be operated so as to control temperature in the concentrated spent liquor, thus allowing optimum operation in the succeeding liquor preheaters.

Spent liquor leaves the evaporators at a caustic concentration of 235 to 255 grams per liter and is pumped to a series of three test tanks where analyses can be made and concentration adjusted as necessary. Make-up caustic is added at this point from a fourth test tank. Three single-stage, centrifugal pumps (*21E*), 2000 gallons per minute, draw liquor from the test tanks, and there are also two spare pumps. These pumps discharge liquor at up to 160° F. and pressure of 225 pounds per square inch to the first in the series of five preheaters associated with each of the three digestion units. Each preheater is fed steam produced in one of the five successive flash tanks located in its associated digestion unit. The preheaters are shell-and-tube heat exchangers, 600 tubes and eight passes (*2E*); besides the 15 in operation there are nine spares, giving 24 preheaters in all. Part of the spent liquor splits off after the first preheat stage and goes to the pug mixers at 200° F. The remainder passes through the next four preheat stages and goes to a set of liquor booster pumps of the same type and number as those following the test tanks. They discharge spent liquor at 300° to 320° F. and a discharge pressure of 300 pounds per square inch to the line feeding the live steam digesters.

Alumina hydrate Is washed and calcined

Alumina hydrate slurry from the primary thickeners is washed in two counter-current decantation washers, 24 feet in diameter and 60 feet high. Washer overflow returns to the primary thickeners, and the underflow goes to nine calcining units arranged in parallel. First on each unit is a rotary vacuum filter (filter cloth inside drum) (*7E*), 12 feet in diameter and 7 feet long, which is fed hydrate slurry plus about one pound of 200° F. wash water per pound of alumina. Filtrate is recycled to the decantation washers. Screw conveyors carry the filtered alumina hydrate to gas-fired rotary kilns (*18E, 19E*), 9.5 feet in diameter and 250 feet long. The kilns operate at 2000° F. and use 2600 B.t.u. to calcine 1 pound of alumina, as follows:

$$Al_2O_3.3H_2O \rightarrow Al_2O_3 + 3H_2O$$

Six kilns discharge calcined alumina to rotary coolers and three to coolers consisting basically of a set of tubes mounted longitu-

Table V. Typical Analysis and Characteristics of Alumina

	%
Al_2O_3	98.35
Na_2O	0.60
Fe_2O_3	0.02
SiO_2	0.02
TiO_2	0.005
Lost on ignition, H_2O	1.00
SIZE RANGE	
+100 mesh	1.0
+200 mesh	50.0
+325 mesh	90.0

PRECIPITATOR FARM

▶

Green liquor entering the precipitator tanks; air lift is mounted along tanks's vertical center line

◀

Precipitator tanks hold green liquor for 36 to 48 hours, while alumina hydrate precipitates on seed crystals of same substance dinally around the kiln discharge end. Both types of coolers are followed by fluosolids coolers which discharge product alumina at 180° F. Each kiln is rated at 350 tons per day of calcined alumina (Table V).

The amounts of raw materials needed to make 1 ton of alumina (Table VI) depend chiefly on the type of ore used and to a lesser though still significant extent on how carefully the process is controlled. Kaiser Aluminum currently recovers about 95% of the available alumina charged to the Baton Rouge digestion system.

Table VI. Raw Materials per Ton of Alumina[a]

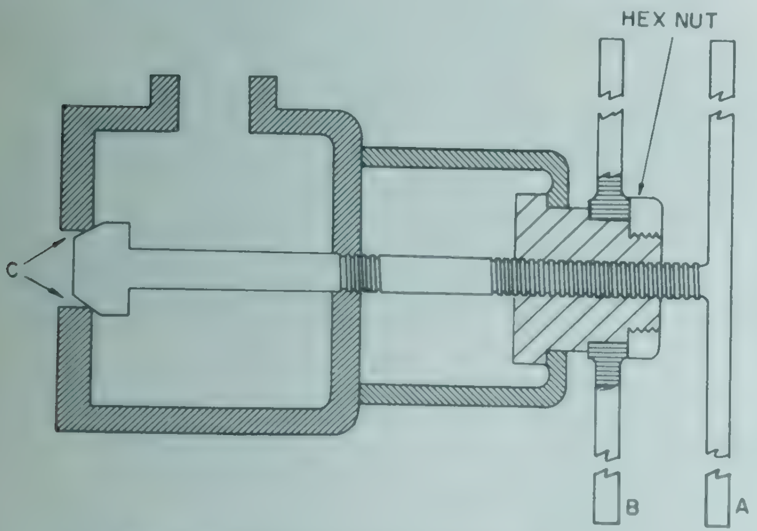
Material	Amount
Bauxite, tons (dry basis)	2.3
Soda ash, pounds	180
Lime, pounds	140
Starch, pounds	11
Fuel, B.t.u.	10,000

[a] From Jamaican bauxite.

Maintenance problems are complex

An alumina plant poses no unusual corrosion problems, and low carbon steel is suitable for most process equipment. But such a plant does handle tremendous quantities of process liquor at high temperatures and pressures and containing large amounts of abrasive solids and scale forming constituents. This, combined with the economic need for a high plant service factor, creates a very complex maintenance problem. Careful planning and management of maintenance services is therefore required.

Valves in particular see very heavy service, and Kaiser uses throughout the plant a valve developed by the industry and modified as necessary to fill specific needs. Basically, it is an ordinary angle valve whose unique feature is that both the valve stem and its mounting nut can be turned. The operator can thus rotate the valve disk against the seat to grind off scale with the valve assembly still in place. A particularly severe valve problem exists at the point where the holding digesters discharge to the flash tanks at 225 pounds per square inch carrying a considerable amount of abrasive solids. A valve that would do the job was not available, and Kaiser finally designed its own.



Schematic diagram of special angle valve

Scale is ground off periodically at C by turning normal operating handle A simultaneously with B

Attainment of working temperature in the live steam digester requires injection of 110,000 to 140,000 pounds per hour of steam at 300 pounds per square inch per operating digester unit. This, too, was a problem. Commercial equipment was available to handle such injections, but only within narrow flow rate limits, beyond which violent steam hammer and unsatisfactory heat transfer developed. Here again Kaiser worked out its own solution, a device which works satisfactorily over a wide throttling range on both steam and liquor.

Process caustic and steam are made on the Baton Rouge plant site. Caustic comes from a standard causticizing plant which reacts sodium carbonate with lime produced by burning oyster shells in rotary kilns. Calcium carbonate resulting from causticization is washed and reburned in the lime kilns. Steam, produced at 850° F. and 850 pounds per square inch, is reduced to process pressures in extraction turbines which generate all electric power needed in the plant. Since more steam is needed for processing than for power production, some of it is reduced to process pressures in desuperheaters.

Special products

In addition to alumina for reduction to aluminum, the Baton Rouge plant produces such special products as calcined, hydrated, and active grade aluminas for chemical, refractory, and abrasives industries.

Calcined alumina is used in the production of abrasives, porcelains, electrical insulators, and high temperature refractories. It is a white, granular material, very hard and extremely inert to chemical attack.

Hydrated alumina is also a white granular material, which is chemically reactive. It is used in the production of catalysts, alums, water treating compounds, enamels, frits, and glazes.

Active grade alumina is a material made up of coarse, white granules ranging in size from 1 inch down to 14 mesh. Because of its large surface area per unit weight, active grade alumina lends itself well to absorbing and drying applications. It is capable of reducing water content of gases to a very low dew point; it also makes an efficient catalyst carrier.

The special products department also produces active grade alumina in the form of pellets. Hydrated alumina is compressed into tablets, which are then made into active grade alumina by controlled calcination. These pellets and tablets are produced primarily for use in production of aluminum fluoride.

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Processing equipment

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(3E) Chicago Bridge & Iron Co., Chicago, Ill., six primary thickeners, special design cone bottom.
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ALUMINUM

Light Metals King

KENNETH M. REESE, Assistant Editor
in collaboration with

A. F. GARCIA AND R. A. LEWIS
Kaiser Aluminum & Chemical Corp., Oakland, Calif.

THE reduction plant of Kaiser Aluminum & Chemical Corp., Chalmette, La., is located on a 280-acre Mississippi River site, 7 miles downstream from New Orleans and some 90 miles south of the Baton Rouge alumina plant. It is thus but a few hours by rail (or water) from the source of its principal raw material. Construction began on the $150,000,000 plant in February 1951. The first primary aluminum was poured in December 1951 and the plant was completed in August 1953. Design capacity is 400,000,000 pounds of primary aluminum a year, more than the annual capacity of the entire United States before World War II. Chalmette is today the largest single alumina reduction plant in the country.

Sixteen parallel buildings, each 960 feet long, house the alumina reduction cells (pots). Each building contains two rows of 36 pots each, and the 72 pots connect electrically in series. Adjacent pairs of buildings also connect in series to give eight separate "potlines," each containing 144 pots, or 1152 pots in all. Nine, 3400-ton capacity, alumina storage silos stand along a line perpendicular to and connecting the midpoints of the longitudinal centerlines of the pot buildings. Alumina from Baton Rouge arrives in hopper cars at the river side of the plant where it drops onto a 2000-foot conveyor belt which carries it to the tops of the silos at a rate of about 150 tons an hour (Figure 1). Smaller silos, with 2000-ton total capacity, store cryolite and aluminum fluoride which may arrive either in bulk or in bags. When in bulk, they, too, are handled by the 2000-foot conveyor belt. From storage, the alumina, cryolite, and aluminum fluoride go directly to the pots (Table I).

The Chalmette plant uses Soderberg reduction cells (7 which feature one continuous, self-baking anode, as opposed to

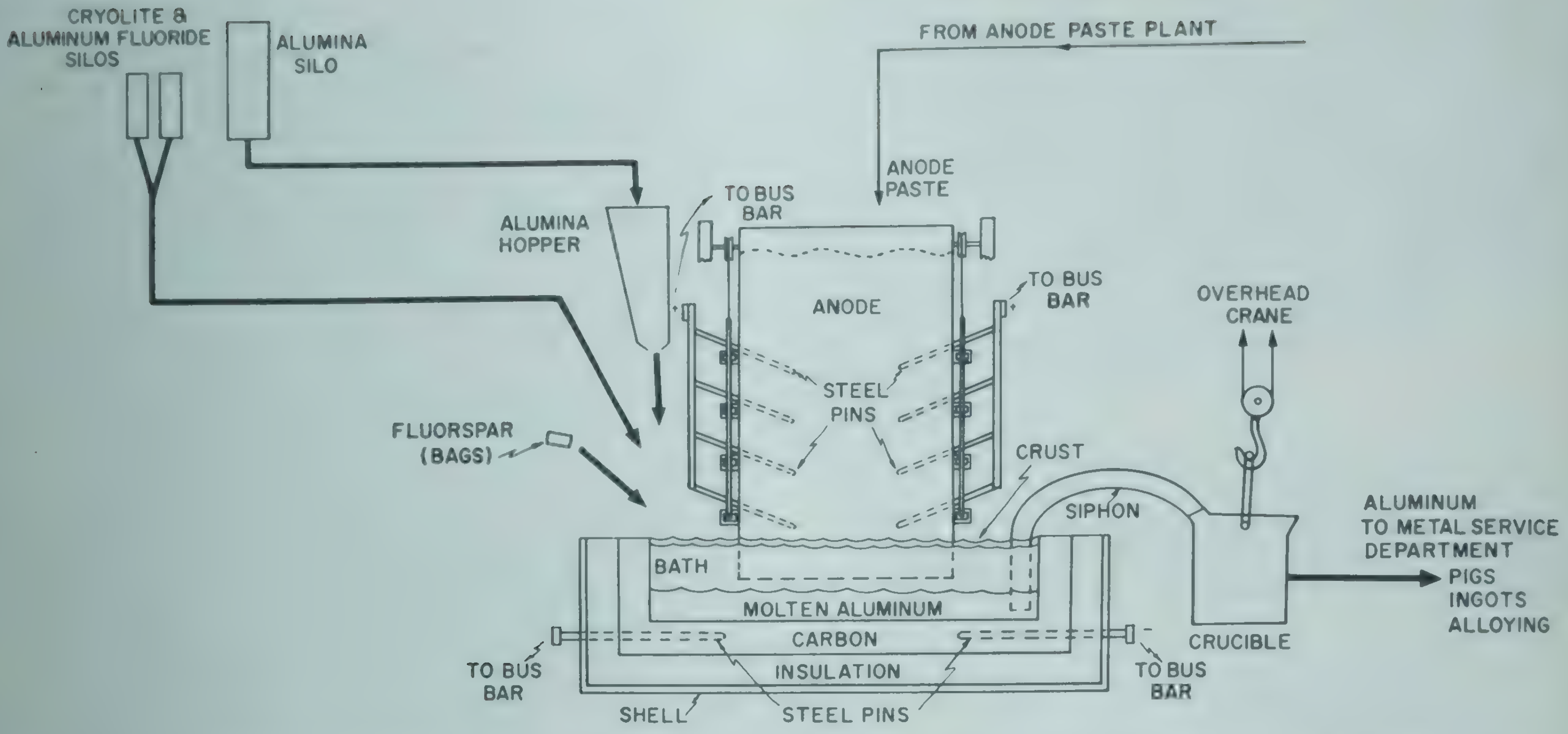


Figure 1. Flow sheet of Soderberg anode paste process at Chalmette, La., plant of Kaiser Aluminum & Chemical Corp.

prebaked anodes which are used in sets, often 24 to a pot. Soderberg anodes were used first in Europe to produce calcium carbide and ferroalloys in the electric furnace and were adapted later to alumina reduction. While they are the newer development of the two, they have not outdated prebaked anodes, which are still used widely in the aluminum industry. Kaiser's Mead, Wash., reduction plant (350,000,000 pounds a year) is a prebake plant, while its Tacoma, Wash., reduction plant (66,000,000 pounds a year) is a Soderberg plant.

Prebaked anodes are usually about 14 × 18 × 11 inches. They are bolted to the lower end of individual anode bars and are raised or lowered individually to maintain proper position with respect to the bath. They are replaced individually as they are consumed. Raw materials used in prebaked anodes are essentially the same as those used in Soderberg anodes. Carbon paste is stamped into green anodes in a hydraulic press, and these are baked in a pit furnace at 1000° C. for about 140 hours. The total baking cycle, including cooling, takes roughly 12 days. A steel connecting stub is inserted into a preformed hole in the top of the finished anode and anchored in place by casting molten iron into the hole around the stub.

Soderberg anode paste at Chalmette is fed into the top of a rectangular steel hopper positioned above the pot. Current enters the anode via rows of steel pins (studs) inserted horizontally through the sides of the hopper and into the paste. (There is also a type of Soderberg anode that uses vertical studs.) Heat conducted from the molten bath and that generated by the passage of current combine to bake the paste as it moves downward through the hopper, so that at a point about 20 inches above the bath surface it has become a monolithic mass of carbon with high electrical conductivity.

Table I. Raw Materials for Aluminum

	Pounds per Pound of Product Aluminum
Alumina (Al_2O_3)	1.93
Cryolite (Na_3AlF_6)	0.025
Aluminum fluoride (AlF_3)	0.025
Fluorspar (CaF_2)	0.0026
Anode paste (carbon)	0.55
Cathode paste (carbon)	0.024

Anodes consumed at one inch per day

In horizontal cross section the anodes are 5 × 16 feet. They are consumed at a rate of about 1 inch of vertical length every 24 hours, and fresh paste is fed to the top of the hopper every 12 days. Anodes weigh about 20 tons, depending upon the amount of make-up paste present in the top of the hopper. They are so supported that they can be moved up and down, sliding freely in the hopper, by the screw jacks used to position them properly in the bath. As an anode is slowly consumed and lowered, the steel studs move downward with it. When the bottom rows of studs approach the molten bath, they are removed with a "stud-puller" and reinserted near the top of the anode. Flexible copper couplings connect the studs to the aluminum bus bar which carries current along the potline.

The Chalmette pots are 10 × 20 feet in outside, horizontal cross section and have an outer shell of $^5/_8$-inch steel plate. About 8 inches of insulation (refractory brick or alumina) line the bottom of the shell, and about 2 inches of insulation line the sides. On top of the insulation is a layer of carbon, 14 inches thick, which serves as the cell lining. (The cell lining is generally called the cathode, although the true cathode is the molten aluminum "pad" that deposits on the bottom of the cell.) The bath cavity is thus about 6.5 feet wide, 18 feet long, and 14 inches deep. Steel pins protruding horizontally through the shell into the carbon lining carry current from the pot, and aluminum couplings connect the pins to the bus.

Pot linings may be either monolithic or made of prebaked carbon blocks joined with carbon cement. Kaiser Aluminum uses monolithic linings. Cathode paste, similar in appearance to bituminous paving, is first tamped into place against a plywood form which rests against the pot insulation. The anode is then lowered to contact a layer of coarse carbon aggregate spread over the paste. Applied current heats the paste to about 800° C. which drives off the volatiles and bakes the lining in place.

A lining may absorb up to its own weight (12 tons) of cryolite during its operating life. Temperature variations cause intermittent expansion and contraction, and the resulting physical movement of the cell can put noticeable bends in the horizontal steel bars which carry current from the lining. In spite of this severe treatment, the Chalmette pots have a 3- to 4-year operating life, and on the average each potline has one pot down for rebuilding at any given time.

Chalmette consumes in an average year some 240,000,000 pounds of anode and cathode pastes, both of which are made at the plant site. Anode paste contains about 30% coal tar pitch and 70% calcined petroleum coke. Cathode paste contains about 15% coal tar pitch and 85% calcined anthracite coal. Paste raw materials (Table II) and formulation must be controlled closely (*4*) since the resulting anodes and cathodes must have good electrical conductivity and erosion resistance (Table III). Anode impurities, chiefly iron and silicon, must be held within rigid limits to avoid contaminating the product aluminum.

Anode and cathode pastes are made in separate equipment, but the methods used are essentially the same. Separate equipment is used primarily for convenience. Calcined petroleum coke for the anode paste plant (Figure 2) arrives in hopper cars which dump it into track hoppers. It is then carried by an inclined belt to storage silos. From storage the calcined petroleum coke is fed to a hammer mill (*6E*) whose product is separated into coarse and medium fractions by a vibrating screen (*7E*). Screened oversize returns to the hammer mill. Part of both the coarse and medium fractions is then split off and fed to a tube mill (*2E*). Tube mill product, after passing through an air classifier (*3E*), is designated the fine coke fraction. Oversize from the air classifier returns to the tube mill. Sieve analyses are run on all three coke fractions at 2-hour intervals.

Coal tar pitch for the anode paste plant arrives in tank cars. It may be heated by feeding steam to coils in the tank car and is then pumped to steam heated storage tanks. The three coke screen fractions are proportioned by automatic batching scales (*8E*) into a steam jacketed blade mixer (*5E*). They are mixed dry for 15 minutes and sampled for screen size. Pitch from storage is then metered (*1E*) into the blade mixer, and batch temperature is raised to about 160° C. at the end of one hour of mixing. When the paste has attained a uniform consistency, it is dumped into transfer cars which carry it to the potlines. The anode paste plant has a capacity of 30 tons of paste per hour.

Potlines operate at 68,000 amperes

Each of the eight potlines at Chalmette operates at 68,000 amperes and 5-volt potential drop per pot. The potential needed to decompose alumina depends upon many variables which include bath composition, electrode activity, cell temperature, alloying constituents in the molten aluminum pad, and current density. Decomposition potential is about 1.7 volts in a Chalmette cell. About 60% of the 5-volt potential drop per pot, then, is due to electrical resistance in the cell and produces heat rather than aluminum.

Much of this heat is needed to maintain the 960° C. operating temperature in the bath, but a significant amount of it can be

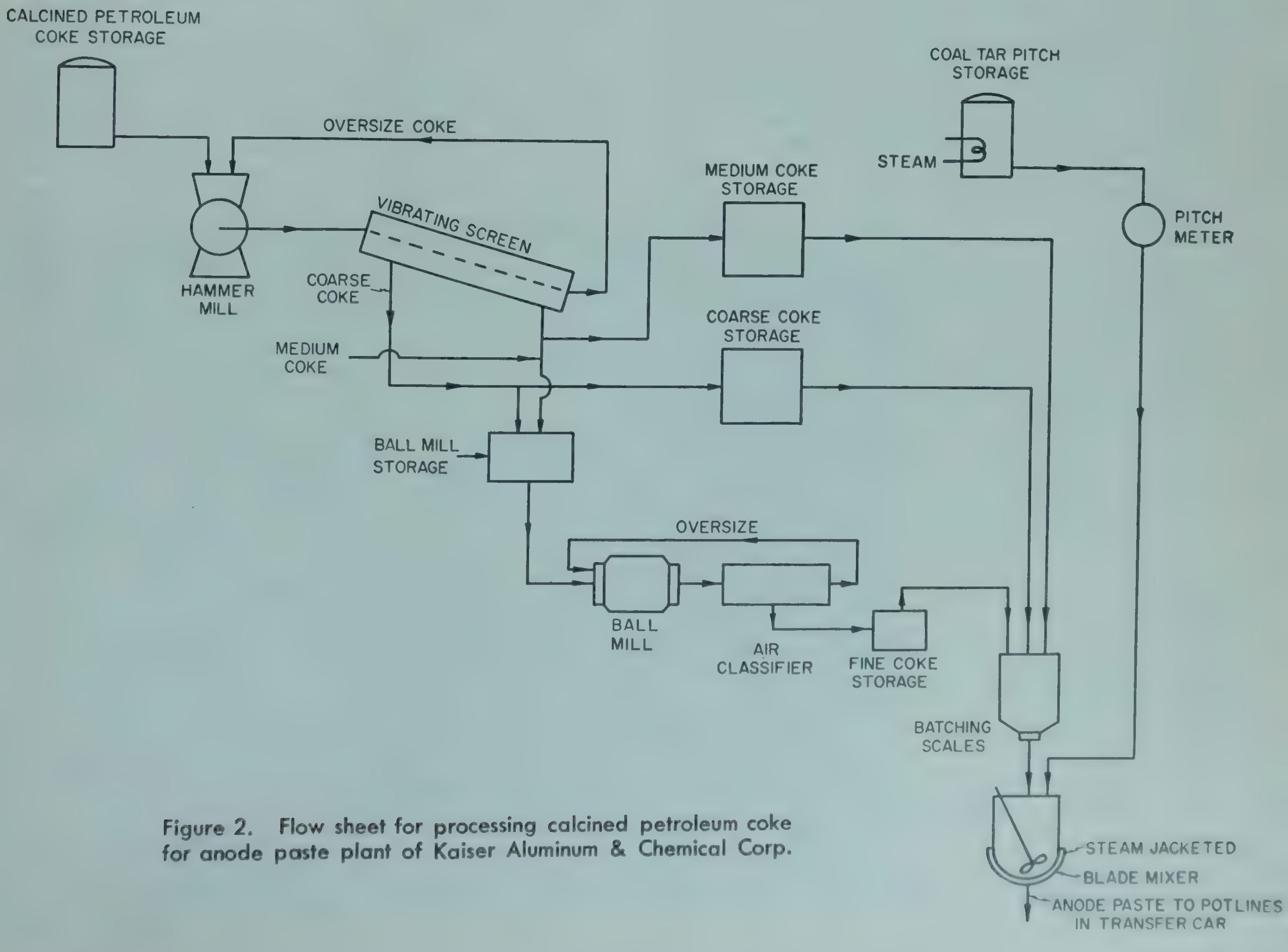


Figure 2. Flow sheet for processing calcined petroleum coke for anode paste plant of Kaiser Aluminum & Chemical Corp.

wasted in the electrical circuits associated with the potlines. Power contributes a large part of aluminum production cost, and it is thus essential that all electric circuits be highly efficient. The aluminum bus bars have very large cross sections and operate at relatively low current density, which means less waste heat generation. Kaiser has developed "copper to aluminum" and "aluminum to aluminum" welding techniques which allow elimination of high-resistance bolted connections at most points in the electric circuits.

Current efficiency in the pots is related directly to bath temperature, so pot insulation must hold this temperature within relatively narrow limits. If bath temperature rises from the desired 960° to 990° C., for instance, current efficiency falls off significantly. During normal operation, a very hard crust forms on top of the bath, and charges of fresh alumina lie on this crust until it is punctured mechanically. Both the crust and the alumina have a noticeable insulating effect, and at times it may be important not to allow a charge of alumina to lie on the crust for too long a time before it enters the bath. Heat generation in the pot goes down with lower anode current density, but this does not mean that lower current density is necessarily desirable, since it is also related to factors like plant amortization. Kaiser uses an anode current density of about 5.8 amperes per square inch at Chalmette.

Theoretically, the amount of aluminum made per unit time in a cell is proportional to the current passing through that cell. Since manpower needed per cell does not increase in direct proportion to cell size, the larger the cell and the higher the current, the lower the cost per pound of aluminum produced. Over a period of years, therefore, the industry has moved toward larger cells and higher currents, and several plants in this country and Europe now operate cells at more than 100,000 amperes (*1*). These are all Soderberg cells, which seem better adapted to higher currents, although prebaked anode cells are operated today at as high as 80,000 amperes. As design current is made larger, however, pot construction and maintenance problems rapidly become more complex, and bigger pots and higher currents cannot be considered definitely advantageous per se.

During normal operation, two distinct layers of molten material are present in the Chalmette pots. On top is the bath proper which is about 8 inches thick and has an approximate specific gravity of 2.15. Its content averages 87% cryolite (which includes the aluminum fluoride), 9% fluorspar, and 4% dissolved alumina. Fluorspar lowers the melting point of cryolite to a desirable range. It also lowers the solubility of alumina in the bath, but at 9% fluorspar content and normal operating temperature the bath will dissolve about 8% of alumina so the effect is not serious. Beneath the bath proper is the molten aluminum pad which has a specific gravity of about 2.29. As electrolysis proceeds, molten aluminum deposits at the top of the pad which grows in thickness from about 4 inches, immediately after the pot is tapped, to a maximum of about 6 inches before it is tapped again. The anode extends into the bath to a point about 2 inches above the aluminum pad.

Table II. Anode Paste Raw Materials

	Coal Tar Pitch	Calcined Petroleum Coke
Ash, %	0.1	0.35
Iron, %	0.02	0.04
Silicon, %	0.01	0.02
Sulfur, %	...	1.5
Water, %	...	0.1
Specific resistivity, ohm-inch	...	0.044
Specific gravity	1.30	2.05
Quinoline insoluble, %	5.0	
Benzene insoluble, %	24.0	
Conradson coking value, %	50.0	
Softening point, ° C.	90.0	
Distillation to 360° C., %	5.0	

Table III. Typical Electrode Properties

	Anode	Cathode
Resistivity, ohm/cubic inch	0.0025	0.0028
Apparent density, grams/cc.	1.50	1.50
Crush strength, lb./sq. in.	4–6000	3–5000

Mobile pneumatic machine breaks crust on top of bath so that fresh alumina can enter

Pots are fed every four hours

Alumina travels from the storage silos to the pots in dump boxes handled by overhead cranes. On each pot are four, 1500-pound-capacity alumina hoppers of a type standard in the industry. The hopper bottoms are equipped with measuring troughs which hold about 30 pounds of alumina. A hand operated chain dumps the trough charge into the pot. When the trough moves to the dumping position, it closes off the bottom of the hopper, so that the remaining alumina cannot run out until the trough is back in position to receive it. An alumina charge of about 330 pounds is fed to the pots at 4-hour intervals, and a pneumatic machine mounted on a small truck breaks the crust on the bath to allow the charge to enter.

Thermal and electrolytic decomposition, absorption of the bath by the cell lining, and vaporization slowly deplete the bath, and it must be made up periodically. The stoichiometric weight ratio of sodium fluoride to aluminum fluoride in cryolite ($3NaF.AlF_3$) is 1.50. Operating experience has shown that maintaining approximately this ratio in the bath provides the most efficient combination. The small amount of sodium oxide (0.60%) contained as an impurity in the alumina reacts with the cryolite and causes a gradual build-up of the bath's sodium fluoride content. Aluminum fluoride is added to the pots as necessary to maintain the bath ratio.

Bath ratio in each pot is checked at about 3-day intervals. A hole is punched in the crust, and a small amount of the bath is dipped out. It hardens quickly to a pellet which is then broken open. Phenolphthalein or bromothymol blue is dripped on the inner surface of the pellet, and the resulting color gives an indication of the bath ratio. This is an approximate method, but an experienced man can use it to estimate the bath ratio within limits at least as narrow as those within which the ratio can be held in practice.

Plant efficiency depends to a great extent upon the skill and experience of the operators. A good pot man can tell from the appearance of the flames over the pot (burning anode gas) whether or not it is operating properly. Anode to cathode distance, about 2 inches, is critical. Too great a distance incurs power waste and too small a distance causes short circuiting within the cell and loss of production. This distance is controlled by raising or lowering the anode so as to maintain the proper voltage drop across the pot. It is roughly self-compensating because as the metal pad grows in thickness, the anode is consumed, and the distance between the two remains approximately constant. Major changes in anode position are ordinarily needed only when the pot is tapped.

"Anode effect," so called, is probably the most noticeable of many imponderables in the alumina reduction cell. It appears when the alumina content of the bath becomes too low. Normally, the gas evolved at a Soderberg anode contains 60 to 75% carbon dioxide, the remainder being chiefly carbon monoxide. Carbon dioxide is probably the primary anode reaction product, but part of it is reduced immediately to carbon monoxide by the anode and by reduction products which form at the cathode and rise through the bath (*3*, *5*).

When anode effect sets in, the normal ratio of carbon dioxide to carbon monoxide approximately reverses, and a significant amount of carbon tetrafluoride begins to evolve. The anode acquires a thin, gaseous film, the bath ceases to wet the anode as it should, and the condition can reach a point at which bath and anode are not in direct contact. Also, the anode may take on a luminous appearance caused by current arcing through the gas film to the bath. Anode effect impedes cell operation seriously. When it comes into play, cell voltage can rise quickly to 40 volts or higher with an accompanying rapid rise in bath temperature.

Fresh alumina stops anode effect

When fresh alumina is added to the cell, anode effect may vanish as quickly as it appeared. A low voltage light bulb is connected across each pot at Chalmette (as elsewhere in the industry). When anode effect sets in, the accompanying voltage rise across the cell causes the bulb to burn brightly and measures are taken immediately to "kill the light," usually by stirring in fresh alumina.

If the alumina content of the bath becomes too high, some alumina will settle to the bottom of the pot (beneath the layer of molten aluminum), which increases electrical resistance and lowers pot efficiency. Also, alumina on the bottom of the pot slowly acquires the characteristics of corundum and does not readily return to the bath and dissolve. Anode effect shows that bath alumina content is too low. It is readily apparent to the operator and can be corrected quickly, which is not the case when alumina content of the bath becomes too high. For many years, therefore, anode effect was allowed to occur at regular intervals of 7 or 8 hours as an indication that the pot was operating properly. Anode effect represents lost production, however, and in present practice bath alumina content is kept high enough so that it occurs only at 2- to 3-day intervals although if it does not appear for an excessively long time in a given pot, that pot is examined carefully for operating discrepancies.

Each pot at Chalmette makes about 1000 pounds of aluminum every 24 hours. At 48-hour intervals, aluminum (2000 pounds) is transferred from the pots to 8000-pound-capacity crucibles handled by overhead crane. These crucibles have tightly fitting lids which mount cast iron spouts. The spout is inserted through the bath crust and into the molten aluminum which is then drawn into the crucible by aspiration. Product aluminum, ranging between 99.6 and 99.9% purity (Table IV), is carried in the crucibles to the metal service department. Here it is cast into pigs of 50 and 1000 pounds or alloyed in gas-fired furnaces and cast into alloy ingots of 6, 10, 15, and 30 pounds. Kaiser Aluminum makes about 10 different alloy pigs and 50 different alloy ingots at Chalmette.

Faraday's law states that 1000 amperes will deposit 0.74 pound of aluminum per hour at 100% current efficiency, and on this basis the Chalmette pots operate at 85 to 88% current efficiency. This is somewhat lower than electrolytic efficiencies achieved in aqueous solutions which frequently approach 100%. The difference is due to a number of factors, chief among them being

Molten aluminum is drawn from pot by aspiration

Steel anode pins show above the spout

Product aluminum is poured into 1000-pound pigs

Chalmette also produces 50-pound pigs and several sizes of alloy ingot

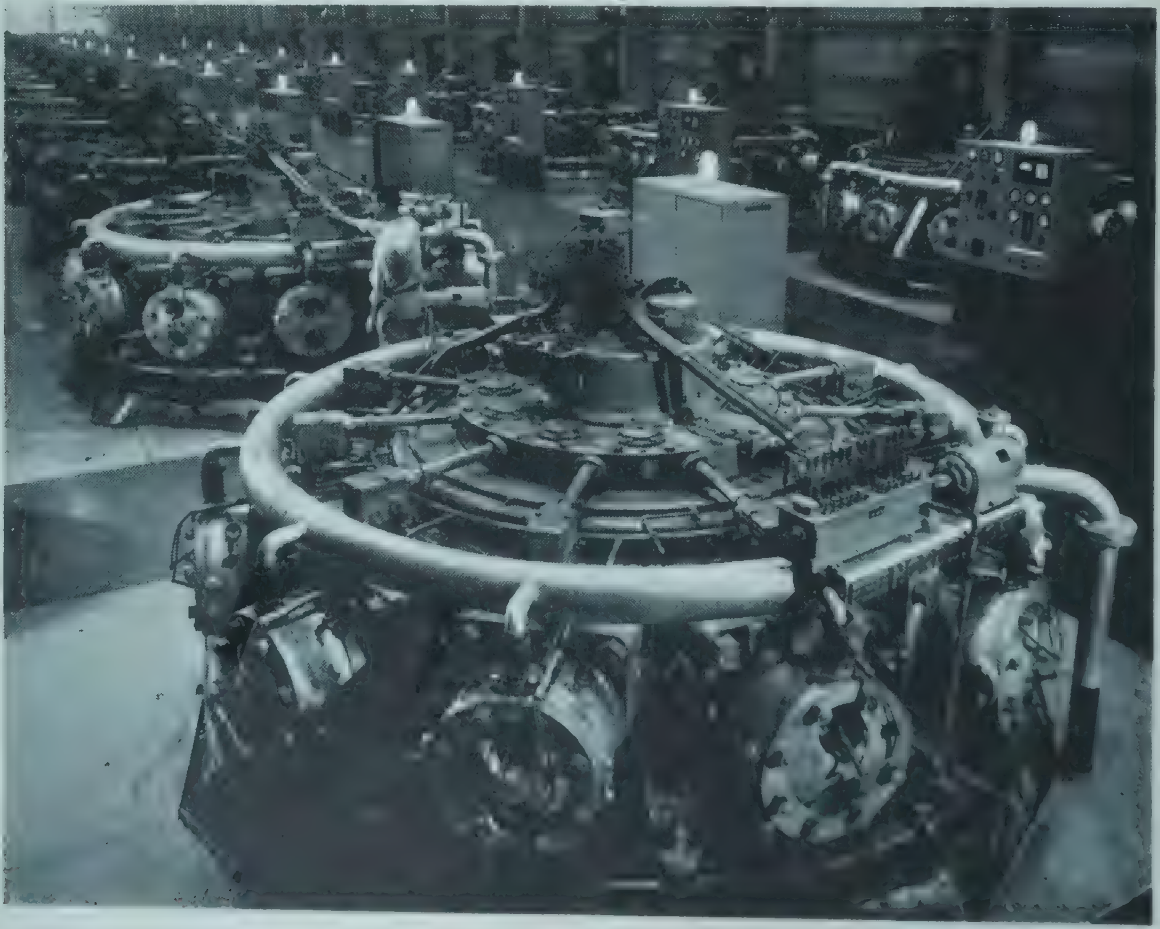
Table IV. Typical Product Analyses

	Aluminum Metal	Typical Ingot Casting Alloys		
		A13[a]	B195[a]	355[a]
Cu	...	0.1	4.0–5.0	1.0–1.5
Si	0.08	11.5–12.5	2.0–3.0	4.5–5.5
Fe	0.12	0.5	0.9	0.4
Mn	...	0.05	0.30	0.30
Mg	...	0.05	0.03	0.4–0.6
Zn	...	0.1	0.30	0.2
Ni	...	0.05	...	...
Sn	...	0.05	...	...
Ti	...	...	0.20	0.2
Others				
Each	...	...	0.05	0.05
Total	...	0.1	0.15	0.15

[a] Designations of Kaiser Aluminum & Chemical Corp.

physical loss and re-oxidation of reduction products formed at the cathode. Over-all cell efficiency at Chalmette averages 8 kw.-hr. (d.c.) per pound of aluminum produced. The entire plant, including the carbon paste plant and electric lights, consumes about 9 kw.-hr. (a.c.) per pound of aluminum produced.

The Chalmette plant generates its own electricity in the largest power plant ever built in the U. S. to serve a single industrial plant. Besides all required alternating current and direct current the power facilities furnish compressed air, domestic water, mill water, and process steam. There are actually two power plants. Two potlines are powered by a pair of gas engine plants, each made up of 40, radial, two-cycle Diesels (*4E*). The gas engine plants together are rated at 103,000 kw. (d.c.). A gas-fired steam-electric plant powers the other six potlines and all other plant equipment. It includes 15 boilers rated at 225,000 pounds per hour of steam at 850 pounds per square inch and 900° F. Fourteen hydrogen cooled generators rated at 25,000 kw. (a.c.) each and two air-cooled units rated at 12,500 kw. each turn out a total of 375,000 kw. (a.c.). Mercury arc rectifiers convert to direct current that part of the steam-electric plant's output which goes to the potlines. The entire power plant consumes some 50,000,000,000 cubic feet of natural gas a year.



Gas-fired, radial Diesels carry part of the reduction plant power load

Aluminum pig is stacked and banded for shipment

At Chalmette each pot is completely enclosed in a hood which has counterweighted side and end access doors. Smoke and particulate matter are exhausted to water scrubbing towers.

Experimental cell located at Permanente, Calif.

The previous description has been limited to a factual portrayal of a modern aluminum reduction plant. It has not emphasized the steady improvement in the process achieved by the industry throughout the years; these improvements have included not only the inherent advantages of larger pots, but also decreases in man-hours, power, carbon, and electrolyte consumption. Unfortunately, experimentation in full-scale potlines is difficult and expensive, and this steady progress has been achieved mainly at the operating level with a minimum of basic research information.

As a more flexible tool for further process improvements, Kaiser has set up a research program at Permanente, Calif., which includes both laboratory studies and pilot-scale development. The latter is carried out in a 10,000-ampere experimental cell where it will be possible to study all operating variables and also to translate laboratory results on an intermediate scale prior to adoption at the production level. The experimental cell is of the prebake type with four anodes. It is a replica of the cells at the Kaiser's Mead, Wash., reduction plant except that it is but one sixth as long. Results of this program have been so encouraging that a second experimental cell is already under construction.

An interesting sidelight to the production of primary aluminum is the refining cell process where lower grades of metal are converted to super-purity aluminum containing a minimum of 99.99% aluminum. Refining to this purity yields a soft, highly reflective, more corrosion-resistant metal. It is made in a three-layer electrolytic cell in which the anode, a molten alloy of aluminum dissolved in copper, is on the bottom. Intermediate is a layer of molten electrolyte, with the cathode of super-purity aluminum at the top.

Although known for many years, this super-purity metal has been produced in only limited quantities, mainly in Europe. Growth of the electronics industry is providing increasing applications for foil, and catalysts for the chemical and petroleum industries are now significant consumers. Because of its unique surface properties and ease of working, it is also finding increased use in costume jewelry and many other decorative applications. Kaiser Aluminum went into commercial production of super-purity metal at its Mead, Wash., reduction plant in mid-1955.

A cliché that during the past 10 years has become well worn in respect to many products might also be applied to aluminum: The future looks bright. Steel-reinforced aluminum cable now carries more than 90% of the high voltage power generated in the U. S. Aluminum foil shipments reached 75,000 tons in 1954, up 30% from 1953. The automobile industry may use twice as much aluminum in 1955 as it did in 1954. These are but a few instances. Total aluminum consumption in the U. S. could double its present rate by 1975 (*2*).

New primary aluminum capacity came on stream to the tune of 605,000 tons in the U. S. during the three years, 1952 through 1954. Anaconda Aluminum Co. dedicated its Columbia Falls, Mont., plant (60,000 tons per year) in August this year. Alcan put 91,500 tons of capacity into operation when it opened its new smelter at Kitimat, B. C., in 1954, and has 240,000 tons of additional annual capacity scheduled or under construction. By early 1956, Alcoa expects to have 65,000 tons of new annual capacity in operation at Point Comfort and Rockdale, Texas. Reynolds has announced an expansion program that will increase its primary aluminum capacity by 135,000 tons a year.

Kaiser Aluminum & Chemical Corp. has established itself solidly in the aluminum industry as a fully integrated producer and like other North American producers is working hard to expand the market for its products. Looking ahead too far is chancey, but looking backward, it is quite certain that Hans Christian Oersted would be amazed at what has happened to his "lump of metal which in color and luster somewhat resembles tin."

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Processing equipment

(1E) Brodie Co., Ralph N , San Leandro, Calif., pitch meter, model B53.
(2E) Kennedy-Van Saun Mfg. & Engineering Corp., New York, N.Y., air swept tube mill, 8 × 14 inches.
(3E) *Ibid.*, radial flow air classifier, 9.5-foot diameter.
(4E) Nordberg Mfg. Co., Milwaukee, Wis., gas-fired radial engines, Type RTG, spark ignition.
(5E) Patterson-Kelley Co., Inc., East Stroudsburg, Pa., Kneadmaster blade mixer, 750 gallons.
(6E) Pennsylvania Crusher Co., Philadelphia, Pa., reversible hammer mill, 36 × 50 inches.
(7E) Tyler Company, The W. S., Cleveland, Ohio, double surface vibrating screen, 4 × 10 feet, Hum-Mer Type 38.
(8E) Yale & Towne Mfg. Co., New York, N.Y., batching scales, 0 to 10,000 pounds, 10-pound graduations.

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